Thermodynamics of Chemical Processes

YU.M. ZHOROV

Petrochemical Synthesis, Processing of Petroleum, Coal, and Natural Gas

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The present book deals with methods of calculating the thermodynamic characteristics of individual substances and petroleum fractions, and also the heats of reactions, equilibrium constants, and equilibrium compositions. It gives the thermodynamic functions of simple substances, hydrocarbons, and their derivatives, as well as the thermodynamic characteristics for basic production processes.

Space is devoted to the employment of the methods of thermodynamics for analysing the mechanism and kinetics of reactions, and the heat regimes of industrial reactors.

The book is intended for scientists, engineers, and technicians employed at institutes and enterprises of the chemical, petrochemical, and related branches of industry.

Contents: Application of Thermodynamic Relations to Calculations of Chemical Processes. Calculations of Heats, Equilibrium Constants, and Equilibrium Compositions of Simple Reactions. Calculation of the Equilibrium Composition of Complex Reactions. Adiabatic Equilibrium Reactions. Calculations of Heats of Industrial Hydrocarbon Treatment Processes. Thermodynamics of Mutual Hydrocarbon Conversion Reactions. Thermodynamics of Reactions of Hydrocarbons and Their Derivatives with the Evolution or Absorption of Hydrogen. Production of Synthesis Gas and Syntheses Based on CO and CO_2. Thermodynamics of Chemical Processes in Natural Gas Treatment. Appendices: Methods of Calculating the Standard Thermodynamic Functions of Hydrocarbons and Their Derivatives. Tables of Standard Thermodynamic Functions for Simple Substances, Selected Inorganic Compounds, Hydrocarbons, and Their Derivatives.

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During recent years, Yuri Zhorov has conducted extensive research related to the thermodynamic analysis of petrochemical processes, and has taught courses on the fundamentals of chemical thermodynamics and its use in industrial chemistry. The present book is based on the data he has gathered in this field and the conclusions he has made.

He is the author of nine monographs and over 300 articles in Soviet and foreign journals. His monographs *Isomerization of Hydrocarbons, Modelling of Physicochemical Processes of Petroleum Refining and Petrochemistry* (both in Russian) and a number of others have been acknowledged by specialists in the USSR and other countries.

Ю.М. Жоров

ТЕРМОДИНАМИКА ХИМИЧЕСКИХ ПРОЦЕССОВ

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Preface

It gives me great pleasure to address the readers of the English translation of my book. I hope it will be helpful when performing thermodynamic calculations or when obtaining data on the thermodynamics of industrially important reactions involved in the processing of petroleum, natural and accompanying gas, coal, and in petrochemical synthesis. I also hope the reference data on the thermodynamic functions of substances and the original and known methods of calculating such functions presented in the book will help the reader in his work.

Although the fundamental methods of calculating the thermodynamic characteristics of chemical reactions and the thermodynamic functions of individual substances or their mixtures needed for this purpose were developed quite long ago, they are constantly being used and, therefore, are being improved. It is impossible to imagine that any researcher or engineer when studying a chemical process will not begin an analysis by acquainting himself with its thermodynamic characteristics such as the heats, entropies, Gibbs energies, and equilibrium compositions, these quantities being considered at various temperatures, pressures, and initial compositions of the reaction mixture. Only such an analysis and the comparison with the results realized in a reactor enable one to estimate the efficiency of a real process, choose an efficient heat regime in the designing stage and, consequently, the proper design of the reactor and technology of the process, and to tackle the problem of improving the existing technology.

The relations of chemical thermodynamics used to perform calculations are very simple, but their derivation may involve some difficulties. Hence, if the reader has no desire to improve these relations and there is no need to demonstrate his knowledge to his instructor, all the derivations can be omitted.

The major part of the considered reactions belong to the broad field of chemistry of conversion of hydrocarbons, their mixtures and comparatively simple derivatives. Nevertheless, the relations contained in the book and the reference data make it possible to analyse a wide range of reactions in organic chemistry.

The thermodynamics of chemical reactions has received a new impetus in connection with the widespread introduction of computers that eliminate the problems of numerical calculations. This is why the thermodynamics of complex multiple-component reactions, the thermodynamics of reactions in real gas mixtures, of new polymerization and polycondensation reactions, of elementary reactions and the like are developing at a tremendous rate. These new achievements have been illustrated to a certain degree in the present book, but it is mainly intended for a broad circle of readers. Hence, the main attention is devoted to a description of various methods, examples of calculations, and to the obtaining of the thermodynamic quantities needed for calculations.

Modern chemical thermodynamics has been created by the work of scientists of many countries. I would like to draw the reader's attention to the contribution of Russian and Soviet scientists. It was exactly in Russia that the fundamental laws of thermochemistry were formulated, while considerably later Soviet scientists developed the thermodynamics of radical reactions, the thermodynamics of the conversions of complex hydrocarbon mixtures, a number of novel methods of calculating thermodynamic functions for temperatures up to 20 000 K, etc.

I have used the International System of Units (SI), which required some changes in setting out the working relations, but made the book available for readers in all countries.

Yuri M. Zhorov

List of Symbols

The symbols in this book are mainly consistent with the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* adopted by the IUPAC Council at Cortina d'Ampezzo, Italy, on July 7, 1969 [*Pure and Applied Chemistry*, **21**, 1 (1970)]. The symbols are generally explained in the text for convenience of reading.

A area; Helmholtz energy
A chemical substance (reactant)
A′ chemical substance (product)
a activity; parameter of van der Waals equation
B chemical substance (reactant)
B′ chemical substance (product)
b constant; parameter of van der Waals equation
C heat capacity
C chemical substance (reactant)
C′ chemical substance (product)
c molar concentration
D chemical substance
d constant; relative density
E energy
f fugacity
G Gibbs energy; mass transfer
g constant
H enthalpy
h caloric coefficient; constant
K equilibrium constant
k number of substances
L number of carbon atoms
M molecular mass
m mass; number of moles
N number
n molar flow; number
P degree of polymerization
P polymer
p number of reactions; partial pressure; pressure
Q heat
q caloric coefficient; heat
R molar gas constant
r constant; number; rate of reaction
S entropy
s standard error

s^2 variance
T absolute temperature (K)
t temperature (°C)
U internal energy
v molar volume
W work
w rate of cracking; rate of polymer growth
X thermodynamic function
x mole fraction
Y mass fraction; mass yield of product
y degree of conversion of a reactant (yield)
Z compression factor
z mass fraction; ratio; unknown quantity
α difference between molar volumes of ideal and real gas
γ fugacity (activity) coefficient
Λ increment
δ increment; ratio; stoichiometric coefficient of solid
$\varkappa$ compressibility
λ chemical variable; mass yield of catalysate
μ chemical potential
ν stoichiometric coefficient
Π degree of polymerization
π reduced pressure
ρ density; stoichiometric coefficient (liquid or solid)
σ symmetry number
τ reduced temperature
Φ thermodynamic function
φ reduced volume

Superscripts

cd condensed
g gas
glq gas-liquid
lq liquid
s solid
v vaporization
° standard state
* ideal state
′ product

Subscripts

a amorphous
ad adiabatic
alk alkanes
b boiling
c coke; combustion; cracking

cat catalytic
cd condensed
comp compression
cr cracking; critical; crystalline
d depolymerization; diluent
dec decomposition
eq equilibrium
ex experimental
exp expansion
ext external
f formation
fin final
for forward
fs feed stock
g gas; growth
h hydrocarbon; hydrogen
hr heavy reflux
ht heating
i *i*-th component
id ideal
in initial
int internal
is iso
le light end
lim limiting
lq liquid
lr light reflux
m melting; mixture
max maximum
mech mechanical
n normal
ol olefins (alkenes)
pr process; product
r reactant
rev reverse
s solid
sat saturated
sub sublimation
v vaporization
0 initial state

The Greek letter Δ in front of a thermodynamic function (for example ΔH) means that the change (final minus initial value) is referred to.

The subscripts p, T, etc. indicate that the quantity they relate to is at constant pressure, temperature, etc., respectively (for example, C_p is the heat capacity at constant pressure).

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Chapter 1

Application of Thermodynamic Relations to Calculations of Chemical Processes

1.1. Fundamental Relations of Chemical Thermodynamics

The thermodynamic calculations of chemical processes are based on the application of the first and second laws of thermodynamics to them. The use of ready formulas contained in the literature for calculations always involves the danger that the wrong figures will be inserted into the wrong formula, and this, while not being noticed by the investigator, leads to a meaningless or incorrect result.

We must also note the fact that the setting out of the fundamentals of thermodynamics is becoming better and better, and today we have to consider a number of textbooks and monographs obsolete. The ways of treating the subject differ quite appreciably for specialists in thermodynamics and physical chemistry.

For this reason, below we give the fundamental relations of chemical thermodynamics.

1.1.1. The First Law of Thermodynamics

Chemical thermodynamics studies the energy transitions attending or causing physicochemical processes. To simplify analysis, these energy transitions are treated for a specific real or mental object—a thermodynamic system (or simply a system). A system that exchanges neither mass nor energy with the surroundings is said to be **isolated.** A thermodynamic system that exchanges only energy is said to be a **closed** one. A system that exchanges both mass and energy is said to be an **open** one.

Mass is obviously exchanged at the expense of either a diffusion (because of the difference in concentrations) or convection (because of the difference in pressures) flow. The exchange of energy is possible by its transfer in the form of heat Q or of work W. Notwithstanding the widespread use of the terms "heat" and "work", their proper understanding is a matter of principle in interpreting the laws of thermodynamics. When energy is transferred in the form of heat, the position of the bodies forming a thermodynamic system, i.e. its shape,

does not change. The energy from one system is transferred in the form of the energy of the disordered motion of microparticles, the temperatures of the systems transmitting and receiving the heat being different. When energy is transferred in the form of work, it can be in one of the following forms: (a) mechanical work when the volume of the system changes; (b) work of the surface tension forces when the external surface changes; (c) work of an electric field; and (d) work of a magnetic field. The performance of work is mainly associated with the ordered motion of microparticles (or their aggregates—bodies) under the action of a force.

The two ways of transferring energy are not equivalent. The work transferred from one thermodynamic system to another can be converted into any kind of energy (kinetic, potential, electrical, etc.). Heat is spent only on a change in the internal energy of a system and is not converted directly into other kinds of energy. Therefore, for example, work can be converted into heat when two bodies interact (rubbing surfaces). Heat can be converted into work only when three bodies interact. They are a heat source, a working body (it changes its volume and performs work), and the consumer of work.

From these standpoints, the application of the widespread term "work of a chemical reaction" calls forth definite objections, and we shall not use it in the following.

We shall limit our treatment to systems in which only mechanical work is done. The basic relations obtained below are given in Table 1.

Let us consider a closed thermodynamic system. A small amount of heat δQ is spent on an elementary change in the internal energy of the system dU and on the performance of a small amount of mechanical work δW_{mech}:

$$\delta Q = dU + \delta W_{\text{mech}} \tag{1.1}$$

Equation (1.1) is an analytical expression of the first law of thermodynamics for closed thermodynamic systems, i.e. it is in essence an analytical expression of the law of energy conservation. In accordance with this expression, the heat supplied to a thermodynamic system and the work done by the system are considered to be positive. The internal energy U is determined by the state of the system. A small change in it is a differential of a function of state. When going over from state 1 to state 2, the change in the internal energy is

$$\Delta U = \int_1^2 dU = U_2 - U_1$$

The quantities Q and W_{mech} are not related to the state of a system in the general case and are determined by external actions. When a process occurs in which a system passes from state 1 to state 2, the

Table 1. **Fundamental Relations of the First Law of Thermodynamics**

Relations	Conditions	System: simple, without a change in the masses of the components	System: complex, with a change in the masses of the components
First law of thermodynamics	General form	$\delta Q = dU + \delta W$	$\delta Q = dU + \delta W$
	Ditto, mechanical work is done	$\delta Q = \begin{cases} dU + p\,dv, & U = U(T, v) \\ dH - v\,dp, & H = H(T, p) \end{cases}$	$\delta Q = \begin{cases} dU + p\,dv, & U = U(T, v, m_1 \ldots) = U(T, v, \lambda) \\ dH - v\,dp, & H = H(T, p, m_1 \ldots) = H(T, p, \lambda) \end{cases}$
	Form of equation with caloric coefficients	$\delta Q = \begin{cases} C_v\,dT + h_v\,dv \\ C_p\,dT + h_p\,dp \end{cases}$	$\delta Q = \begin{cases} C_v\,dT + h_v\,dv + \sum_i \left(\frac{\partial U}{\partial m_i}\right)_{T,v} dm_i = \\ \quad = C_v\,dT + h_v\,dv + \left(\frac{\partial U}{\partial \lambda}\right)_{T,v} d\lambda \\ C_p\,dT + h_p\,dp + \sum_i \left(\frac{\partial H}{\partial m_i}\right)_{T,p} dm_i = \\ \quad = C_p\,dT + h_p\,dp + \left(\frac{\partial H}{\partial \lambda}\right)_{T,p} d\lambda \end{cases}$
Corollaries of the first law	Hess's law	$Q_v = \Delta U,\ Q_p = \Delta H$	$Q_v = \Delta U,\ Q_p = \Delta H$ $Q = \begin{cases} \text{(sum of heats of combustion of reactants)} - \\ \quad - \text{(sum of heats of combustion of products)} \\ \text{(sum of heats of formation of products)} - \\ \quad - \text{(sum of heats of formation of reactants)} \\ \text{(sum of binding energies of reactants)} - \\ \quad - \text{(sum of binding energies of products)} \end{cases}$
	Expressions of derivatives of U and H	$\left(\frac{\partial U}{\partial T}\right)_v = C_v$	$\left(\frac{\partial U}{\partial T}\right)_{v, m_i} = C_v,\ \left(\frac{\partial \Delta U}{\partial T}\right)_{v,\lambda} = \Delta C_v$
		$\left(\frac{\partial U}{\partial v}\right)_T = h_v - p$	$\left(\frac{\partial U}{\partial v}\right)_{T, m_i} = h_v - p,\ \left(\frac{\partial \Delta U}{\partial v}\right)_{T,\lambda} = \Delta(h_v - p)$
		$\left(\frac{\partial H}{\partial T}\right)_p = C_p$	$\left(\frac{\partial H}{\partial T}\right)_{p, m_i} = C_p,\ \left(\frac{\partial \Delta H}{\partial T}\right)_{p,\lambda} = \Delta C_p$
		$\left(\frac{\partial H}{\partial p}\right)_T = h_p + v$	$\left(\frac{\partial H}{\partial p}\right)_{T, m_i} = h_p + v,\ \left(\frac{\partial \Delta H}{\partial p}\right)_{T,\lambda} = \Delta(h_p + v)$

expenditure of heat is $Q = \int_1^2 \delta Q$, and the amount of work is $W_{mech} = \int_1^2 \delta W_{mech}$.

The state of a system is determined by **thermodynamic functions.** These are measurable or calculated quantities that can change when a system passes from one state to another (pressure, temperature, concentration, energy, and so on). If X is a thermodynamic function, in any process $1 \rightarrow 2$ it varies continuously (X can change by an infinitely small quantity dX), and the integral $\int_1^2 dX = X_2 - X_1$ does not depend on the transition path. Thermodynamic functions are divided into **intensive** ones (not depending on the mass of the system such as the temperature and concentration) and **extensive** ones (their value is directly proportional to the mass of the system; among them are the volume and energy).

It is important that to characterize the state of a system, it is sufficient to know only a part of the thermodynamic functions, namely, independent functions (arguments, parameters), for example, $X_1, \ldots, X_k$. Any other function X_{k+1} can be expressed as follows: $X_{k+1} = \varphi(X_1, \ldots, X_k)$. For example, for an ideal monatomic gas, it is sufficient to know p and T for calculating the molar volume ($v = RT/p$), molar energy ($E = 3RT/2$), heat capacity ($C_v = 3R/2$), and other quantities.

Experiments show that if system I is in thermal equilibrium with system II, and system II with system III, there is equilibrium between systems I and III. This statement is sometimes called the **zero law of thermodynamics** because the fact that the temperature is an intensive function determining thermal equilibrium is a corollary of it.

If two simple thermodynamic systems are in equilibrium, no exchange of heat (or of any other) energy occurs between them. This is possible if the two systems have the same temperature. Thus, the temperature is an important thermodynamic function determining the possibility and direction of heat energy transfer. Similarly, the pressure determines kinetic, and the concentration, chemical equilibrium. Since $\delta W_{mech} = p\,dv$, Eq. (1.1) can be written in the form

$$\delta Q = dU + p\,dv \tag{1.2}$$

The internal energy of a thermodynamic system that is a simple substance (a simple system) is determined by two parameters (arguments) of state, for example, $U = U(T, v)$. If a system includes several substances and their masses $m_1, m_2, \ldots$ change as a result of a chemical reaction (such a system is called a **complex** one), the quan-

tity U is determined additionally by the masses m_1, m_2, ... of the components: $U = U(T, v, m_1, m_2, \ldots)$, and, consequently,

$$dU = \left(\frac{\partial U}{\partial T}\right)_{v,\, m_i} dT + \left(\frac{\partial U}{\partial v}\right)_{T,\, m_i} dv + \sum \left(\frac{\partial U}{\partial m_i}\right)_{T,\, v} dm_i$$

Two forms of writing a stoichiometric equation are used in the literature [1-4] and in this book.

In the traditional form $(\sum \nu_i A_i)_r \rightarrow (\sum \nu_i' A_i')_{pr}$, all the stoichiometric coefficients are positive and, for example, an isomerization reaction is written as $n\text{-}C_4H_{10} \rightarrow iso\text{-}C_4H_{10}$. For this form, the change in the number of moles during the reaction is $\Delta\nu = (\sum \nu_i')_{pr} - (\sum \nu_i)_r$, and the equilibrium constant is $K_p = (\prod p_i'^{\nu_i'})_{pr}/(\prod p_i^{\nu_i})_r$. A stoichiometric equation is also written in the form $\sum \nu_i A_i = 0$, or for our example of isomerization, $n\text{-}C_4H_{10} + iso\text{-}C_4H_{10} = 0$. It is assumed in this form that the coefficients ν_i are negative for reactants and positive for products. Here $\Delta\nu = \sum \nu_i$ and $K_p = \prod p_i^{\nu_i}$.

It can be seen that the second form enables one to write the expressions for $\Delta\nu$, the equilibrium constants, and also some others more concisely. This is why it is used in the analysis of complex reactions.

If one or two reactions are being investigated, the traditional first form is preferable. Indeed, the equation $A \rightarrow A'$ is shorter than $-A + A' = 0$.

In the following, the form of writing a reaction equation will be clear from the text.

It should be noted that for a chemical reaction proceeding, for example, by the equation

$$\nu_1 A_1 + \nu_2 A_2 + \ldots \rightarrow \nu_1' A_1' + \nu_2' A_2' + \ldots$$

(where ν_i is the stoichiometric coefficient of substance A_i), the changes in the masses of the components Δm_i cannot be arbitrary. It is obvious that

$$-\frac{\Delta m_1}{\nu_1} = -\frac{\Delta m_2}{\nu_2} = \ldots = \frac{\Delta m_1'}{\nu_1'} = \frac{\Delta m_2'}{\nu_2'} = \ldots = \Delta\lambda$$

A change in λ (it is called the **chemical variable**) determines the fraction a component forms of the stoichiometric amount entering into a reaction or formed as a result of it. Before a reaction begins, $\lambda = 0$, and after transformation of the stoichiometric amounts, $\Delta\lambda = \lambda = 1$. For any component i, its instantaneous amount m_i is determined by the arbitrarily chosen amount $m_{i,0}$ before the beginning of the reaction and by the value of λ.

Thus, for a complex thermodynamic system with a chemical reaction, we can go over from the condition $U = U(T, v, m_1, m_2, \ldots)$

to $U = U(T, v, \lambda)$, and therefore

$$dU = \left(\frac{\partial U}{\partial T}\right)_{v,\lambda} dT + \left(\frac{\partial U}{\partial v}\right)_{T,\lambda} dv + \left(\frac{\partial U}{\partial \lambda}\right)_{T,v} d\lambda$$

Introducing this expression into Eq. (1.2) for the arguments T, v, and λ, we have:

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_{v,\lambda} dT + \left(\frac{\partial U}{\partial v}\right)_{T,\lambda} dv + p\,dv + \left(\frac{\partial U}{\partial \lambda}\right)_{T,v} d\lambda \qquad (1.3)$$

If we write Eq. (1.3) in the form of an equation with caloric coefficients, i.e.

$$\delta Q = C_v\,dT + h_v\,dv + q_v\,d\lambda$$

we obtain

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{v,\lambda}, \quad h_v = \left(\frac{\partial U}{\partial v}\right)_{T,\lambda} + p, \quad q_v = \left(\frac{\partial U}{\partial \lambda}\right)_{T,v}$$

When considering the processes at p = const, we shall find it convenient to go over to a new function of state—the enthalpy $H = U + pv$. Therefore

$$dH = dU + p\,dv + v\,dp$$

and

$$\delta Q = dU + p\,dv = (dH - p\,dv - v\,dp) + p\,dv = dH - v\,dp \qquad (1.4)$$

in addition,

$$H = H(T, p, \lambda)$$

and

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p,\lambda} dT + \left(\frac{\partial H}{\partial p}\right)_{T,\lambda} dp + \left(\frac{\partial H}{\partial \lambda}\right)_{T,p} d\lambda \qquad (1.5)$$

Inserting (1.5) into (1.4) we obtain

$$\delta Q = \left(\frac{\partial H}{\partial T}\right)_{p,\lambda} dT + \left[\left(\frac{\partial H}{\partial p}\right)_{T,\lambda} - v\right] dp + \left(\frac{\partial H}{\partial \lambda}\right)_{T,p} d\lambda \qquad (1.6)$$

Equations (1.2) and (1.3) are used for calculations of chemical processes at T and v = const, and Eqs. (1.4) and (1.6), for calculations of processes at T and p = const. It follows from (1.3) that

$$\left(\frac{\partial Q}{\partial T}\right)_{v,\lambda} = \left(\frac{\partial U}{\partial T}\right)_{v,\lambda} = C_v$$

The quantity C_v determines the expenditure of heat needed to change the temperature of a thermodynamic system by unity when the temperature, volume, and composition of the system are constant. It is the heat capacity of the system at a constant volume.

It follows from (1.6) that

$$\left(\frac{\partial Q}{\partial T}\right)_{p,\lambda} = \left(\frac{\partial H}{\partial T}\right)_{p,\lambda} = C_p$$

The quantity C_p determines the expenditure of heat needed to change the temperature of a thermodynamic system by unity when the temperature and pressure are constant. It is the heat capacity of the system at constant pressure.

If we write (1.6) in the form of an equation with caloric coefficients

$$\delta Q = C_p\, dT + h_p\, dp + q_p\, d\lambda$$

we obtain

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,\lambda}, \quad h_p = \left(\frac{\partial H}{\partial p}\right)_{T,\lambda} - v, \quad q_p = \left(\frac{\partial H}{\partial \lambda}\right)_{T,p}$$

1.1.2. Thermochemistry

Thermochemical calculations are based on the application of relations ensuing from the first law of thermodynamics to chemical processes. The fundamental law of thermochemistry—Hess's law, can be substantiated as follows.

Since $\delta Q = dU + p\, dv$, then at constant volume we have

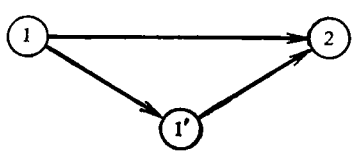
$$Q_v = U_2 - U_1 = \Delta U$$

Similarly, from the condition that $\delta Q = dH - v\, dp$, it follows that at constant pressure we have

$$Q_p = H_2 - H_1 = \Delta H$$

Thus, *at constant volume or constant pressure, the heat of a process depends only on the initial* (subscript 1) *and final* (subscript 2) *states of a thermodynamic system, but not on the path of the transition.*

This statement, known as Hess's law, enables us to calculate the heats of reactions from the heats of other ones and reduces the volume of experimental investigations needed for measuring the heat effects. Assume that a chemical process can occur from state 1 to state 2 in two ways, namely, either directly, or via an intermediate state 1′, as shown in the following scheme:



Assume further, as previously, that $\Delta U = U_2 - U_1$ and $\Delta H = H_2 - H_1$. Moreover, $\Delta U_{1'1} = U_{1'} - U_1$, $\Delta U_{21'} = U_2 - U_{1'}$, $\Delta H_{1'1} = H_{1'} - H_1$, and $\Delta H_{21'} = H_2 - H_{1'}$. It is obvious that $\Delta U = \Delta U_{1'1} + \Delta U_{21'}$, and $\Delta H = \Delta H_{1'1} + \Delta H_{21'}$. Consequently, using the heats of stages 1-1′ and 1′-2, we can calculate the heat of the transition 1-2 we are interested in. In practical calculations, this is done by using the following procedures.

A. From the heats of combustion of the reactants, i.e. from the heats of their oxidation to CO_2, $H_2O_{(lq)}$, N_2, SO_2, hydrogen halides. Let 1′ in the scheme be the combustion products of systems 1 and 2. Hence:

Heat of reaction = (sum of heats of combustion of reactants)
— (sum of heats of combustion of products)

The heat of combustion of an individual substance at 101 325 Pa ($\approx$ 0.1 MPa or 1 atm) (standard pressure) and 298 K is called the **standard enthalpy of combustion** ΔH_c°. Its values for various substances are given in thermodynamic tables of standard values (standard tables). They are related to one mole of the relevant substance, therefore when calculating the sums of the heats of combustion, one must take into consideration the numbers of moles of the reactants.

B. From the heats of formation of the reactants from simple substances (graphite, H_2, O_2, N_2, and so on). Let 1′ in the scheme be simple substances. Hence:

Heat of reaction = (sum of heats of formation of products)
— (sum of heats of formation of reactants)

The heat of formation of a compound from simple substances at standard pressure and 298 K is called the **standard enthalpy of formation** ΔH_f°. Its values are given in standard thermodynamic tables. They are related to one mole of the substance formed, therefore when calculating the sums of the heats of formation, one must take into consideration the number of moles of the reactants.

C. From the mean bond energies, i.e. from the energies of breaking of all the identical bonds in a molecule so that the sum of all the bond energies for a molecule equals the heat of its atomization. If 1′ signifies atoms in the scheme, then

Heat of reaction = (sum of mean bond energies of reactants)
— (sum of mean bond energies of products)

In this case too, stoichiometry must be taken into consideration when calculating the sums. The mean bond energies are given in thermodynamic tables. They are related to the Avogadro constant of identical bonds (to a "mole" of bonds). Owing to the low accuracy of determining the bond energies for bonds in which carbon participates, the tabulated values are usually not related to any specific values of the temperature or pressure.

The conditions that $Q_v = \Delta U$ and $Q_p = \Delta H$ enable one to readily establish the relations between Q_p and Q_v. Since at constant pressure we have $\Delta H = \Delta U + p\Delta v$, then if as a result of a reaction the volume of the system does not change, $\Delta H = \Delta U$. True, this is observed with a certain approximation for reactions in condensed phases, and also for reactions in gases proceeding without a change in the number of moles.

For isothermal reactions in an ideal gas mixture, $p\Delta v = \Delta\nu RT$ and $\Delta H = \Delta U + \Delta\nu RT$ (where $\Delta\nu$ is the change in the number of moles in a reaction).

The temperature dependence of the heat of a reaction (the internal energy of the reaction $\Delta U = Q_v$ or the enthalpy of the reaction $\Delta H = Q_p$) is determined by the temperature dependence of U or H. Since for a thermodynamic system we have

$$\left(\frac{\partial U}{\partial T}\right)_v = C_v, \quad \left(\frac{\partial H}{\partial T}\right)_p = C_p$$

then

$$\left(\frac{\partial \Delta U}{\partial T}\right)_{v,\lambda} = \Delta C_v, \quad \left(\frac{\partial \Delta H}{\partial T}\right)_{p,\lambda} = \Delta C_p$$

Here ΔC_v and ΔC_p are the differences between the heat capacities of the final (products) and initial (reactants) thermodynamic systems.

The relation between ΔU and ΔH has been determined above, therefore the value of ΔH is usually found in calculations. We have

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta C_p \, dT$$

The temperature dependence of C_p and ΔC_p is generally obtained in the form of empirical equations (usually polynomial ones) such as

$$C_p = a + bT + cT^2 + \frac{d}{T}$$

Hence,

$$\Delta H_T = \Delta H_{T_0} + \Delta a\,(T - T_0) + \frac{\Delta b}{2}\,(T^2 - T_0^2) + \frac{\Delta c}{3}\,(T^3 - T_0^3) + \Delta d \ln\frac{T}{T_0}$$

If the mean heat capacities $\overline{C}_p$ (constant within the interval from T_0 to T) are given, we have

$$\Delta H_T = \Delta H_{T_0} + \Delta\overline{C}_p\,(T - T_0)$$

The dependence of the heat of a reaction on the pressure (or volume) is determined by the dependence of H (or U) on p (or v). Since

$$\left(\frac{\partial H}{\partial p}\right)_T = h_p + v$$

$$\left(\frac{\partial \Delta H}{\partial p}\right)_T = \Delta\,(h_p + v)$$

for h_p we have

$$h_p = -T\left(\frac{\partial v}{\partial T}\right)_p$$

Therefore

$$\left(\frac{\partial \Delta H}{\partial p}\right)_{T,\lambda} = -T\left(\frac{\partial \Delta v}{\partial T}\right)_p + \Delta v$$

where Δv is the difference between the volumes of the final (products) and initial (reactants) thermodynamic systems.

Integration yields

$$\Delta H_p = \Delta H_{p_0} + \int_{p_0}^{p} \left[-T \left(\frac{\partial \Delta v}{\partial T} \right)_{p,\lambda} + \Delta v \right] dp \qquad (1.7)$$

For a reaction in an ideal gas mixture, we have

$$\Delta v = \frac{\Delta \nu RT}{p}, \qquad -T \left(\frac{\partial \Delta v}{\partial T} \right)_{p,\lambda} + \Delta v = 0$$

and the heat of the reaction does not depend on the pressure.

For reactions in condensed phases with a minor change in the pressure, we have $\Delta v \approx 0$ and $(\partial \Delta v / \partial T)_{p,\lambda} \approx 0$. Therefore, the enthalpy of such a reaction does not virtually depend on the pressure.

1.1.3. The Second Law of Thermodynamics

The second law of thermodynamics introduces a new function of state, namely, the **entropy** S. It shows that for a closed thermodynamic system all of whose points have the same temperature T, the following relation holds:

$$dS \geqslant \frac{\delta Q}{T} \qquad (1.8)$$

For non-equilibrium (real) processes, we have $dS > \delta Q/T$, while for equilibrium (infinitely slow) processes $dS = \delta Q/T$.

Processes in a closed system can either increase the entropy ($\delta Q > 0$, processes with the supply of heat) or decrease it ($\delta Q < 0$, processes with the removal of heat). However, in an isolated system ($\delta Q = 0$) in which only spontaneous processes of transition from a non-equilibrium state to an equilibrium one can occur, $dS \geqslant 0$. Hence, a non-equilibrium spontaneous process in an isolated system occurs with an increase in the entropy.

We shall be interested in non-equilibrium processes in which a thermodynamic system passes over from a non-equilibrium (for example, an arbitrary mixture of reactants) to an equilibrium (an equilibrium mixture of reactants) state. A glance at Eq. (1.8) reveals that for a non-equilibrium process $T\,dS - \delta Q > 0$. If we introduce the notation $T\,dS - \delta Q = \delta Q'$, the following expression holds:

$$T\,dS = \delta Q + \delta Q' \qquad (1.9)$$

where $\delta Q' \geqslant 0$. The quantity $\delta Q'$ arises in a system owing to the occurrence of non-equilibrium processes in it; for an equilibrium process, $\delta Q' = 0$. Clausius called $\delta Q'$ the uncompensated heat.

Introducing δQ into Eq. (1.9) according to the first law of thermodynamics, we find:

$$T\,dS = dU + p\,dv + \delta Q' \tag{1.10a}$$

$$T\,dS = dH - v\,dp + \delta Q' \tag{1.10b}$$

Equations (1.9) and (1.10) unite the expressions of the first and second laws of thermodynamics. They are what we call the generalized forms of writing the laws of thermodynamics.

From Eq. (1.10a) at constant T and v, we have

$$\delta Q' = -dU + T\,dS = -d(U - TS) = -dA \tag{1.11a}$$

and from (1.10b) at constant T and p:

$$\delta Q' = -dH + T\,dS = -d(H - TS) = -dG \tag{1.11b}$$

The second law of thermodynamics makes it possible to introduce new important functions of state, namely the **Helmholtz energy** $A = U - TS$ and the **Gibbs energy** $G = H - TS = U + pv - TS = A + pv$. The quantities A and G are convenient for determining whether processes are possible in non-isolated systems. For spontaneous non-equilibrium processes at T, v = const, the expression $dA = -\delta Q' < 0$ holds, and at T, p = constant, the expression $dG = -\delta Q' < 0$, i.e. A and G diminish in spontaneous non-equilibrium processes.

Conditions of Equilibrium. One can use the functions of state S, A, and G for determining the thermodynamic possibility of the occurrence of a process. But it is clear from the above that the functions A and G are more convenient for this purpose than S. The matter is that in a spontaneous (i.e. thermodynamically possible) process the entropy grows only if the process is conducted in an isolated system, which is difficult to realize in an experiment. The quantities A and G decrease in thermodynamically possible processes conducted under readily realizable conditions, namely, T, v = const (for A) or T, p = const (for G), the system not being isolated.

Let us now consider a system in which the masses of the components can change both at the expense of only a physicochemical process (closed systems) or at the expense of an exchange of mass with the surroundings (open systems). We can consider that the thermodynamic functions exist regardless of whether the system is closed or open because only one value of U, H, A, and G can correspond to a definite set of T, v, m_1, m_2, . . . or T, p, m_1, m_2, . . . regardless of the path followed in obtaining this set. Consequently, we can also use the conditions $dA \leqslant 0$ (at T, v = const) and $dG \leqslant 0$ (at T, p = const) for open systems.

It follows from the definition of A (i.e. $A = U - TS$) that

$$dA = dU - T\,dS - S\,dT$$

Inserting into this equation the expression for dU from (1.10a), we find:

$$dA = -S\,dT - p\,dv - \delta Q' \tag{1.12a}$$

Similarly from the definition of G (i.e. $G = U + pv - TS$), we have:

$$dG = dU + p\,dv + v\,dp - T\,dS - S\,dT$$

Inserting into this equation the expression for dU from (1.10a), we find:

$$dG = -S\,dT + v\,dp - \delta Q' \tag{1.12b}$$

It should be noted that conditions (1.12) hold for any processes. They are therefore more general than conditions (1.11) which follow from (1.12) as particular cases if T, v or T, p are constant.

Thus, the general conditions for equilibrium are as follows:

(a) in an isolated system, the entropy is constant and maximum ($dS = 0$, $d^2S < 0$);

(b) the Helmholtz energy in a system at T, v = const is constant and minimum ($dA = 0$, $d^2A > 0$);

(c) the Gibbs energy in a system at T, p = const is constant and minimum ($dG = 0$, $d^2G > 0$).

Let us now discuss what can increase $\delta Q'$ in processes at T, v or T, p = const. If conditions (1.12) are applied to a chemical process, the changes in the system are produced by a change in the masses of the components. At constant masses m_i of the components or, which is the same, at a constant value of λ, no changes occur in the system, and $\delta Q' = 0$. It therefore follows from conditions (1.10)-(1.12) that

$$\left(\frac{\partial U}{\partial S}\right)_{v,m_i} = \left(\frac{\partial U}{\partial S}\right)_{v,\lambda} = T, \qquad \left(\frac{\partial U}{\partial v}\right)_{S,m_i} = \left(\frac{\partial U}{\partial v}\right)_{S,\lambda} = -p \tag{1.13a}$$

$$\left(\frac{\partial H}{\partial S}\right)_{p,m_i} = \left(\frac{\partial H}{\partial S}\right)_{p,\lambda} = T, \qquad \left(\frac{\partial H}{\partial p}\right)_{S,m_i} = \left(\frac{\partial H}{\partial p}\right)_{S,\lambda} = v \tag{1.13b}$$

$$\left(\frac{\partial A}{\partial T}\right)_{v,m_i} = \left(\frac{\partial A}{\partial T}\right)_{v,\lambda} = -S, \quad \left(\frac{\partial A}{\partial v}\right)_{T,m_i} = \left(\frac{\partial A}{\partial v}\right)_{T,\lambda} = -p \tag{1.13c}$$

$$\left(\frac{\partial G}{\partial T}\right)_{p,m_i} = \left(\frac{\partial G}{\partial T}\right)_{p,\lambda} = -S, \quad \left(\frac{\partial G}{\partial p}\right)_{T,m_i} = \left(\frac{\partial G}{\partial p}\right)_{T,\lambda} = v \tag{1.13d}$$

Conditions (1.13) reveal that for complex thermodynamic systems, it is convenient to consider the thermodynamic functions for the following arguments—"parameters" of state:

internal energy: $U = U(S, v, m_i) = U(S, v, \lambda)$

enthalpy: $H = H(S, p, m_i) = H(S, p, \lambda)$

Helmholtz energy: $A = A(T, v, m_i) = A(T, v, \lambda)$

Gibbs energy $G = G(T, p, m_i) = G(T, p, \lambda)$

Therefore, for example, for the internal energy, we have:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{v,\, m_i} dS + \left(\frac{\partial U}{\partial v}\right)_{S,\, m_i} dv + \sum \left(\frac{\partial U}{\partial m_i}\right)_{S,\, v} dm_i \quad (1.14a)$$

A new function $(dU/dm_i)_{S,\, v}$ has appeared in Eq. (1.14a). It is designated by μ_i and is called the **chemical potential.** This is why Eq. (1.14a) is more often written in the form

$$dU = \left(\frac{\partial U}{\partial S}\right)_{v,\, m_i} dS + \left(\frac{\partial U}{\partial v}\right)_{S,\, m_i} dv + \sum_i \mu_i\, dm_i \quad (1.14b)$$

or, with a view to the expressions $(\partial U/\partial S)_{v,\, m_i} = T$ and $(\partial U/\partial v)_{S,\, m_i} = -p$:

$$dU = T\, dS - p\, dv + \sum \mu_i\, dm_i \quad (1.14c)$$

It follows from the definition of the function $A = U - TS$ that

$$dA = dU - T\, dS - S\, dT$$

or with a view to (1.14c):

$$dA = -S\, dT - p\, dv + \sum_i \mu_i\, dm_i \quad (1.15)$$

It follows from the definition of the function $G = U + pv - TS$ that

$$dG = dU + p\, dv + v\, dp - T\, dS - S\, dT$$

or with a view to (1.14c):

$$dG = -S\, dT + v\, dp + \sum_i \mu_i\, dm_i \quad (1.16)$$

Hence, the chemical potentials μ_i are functions of state of a thermodynamic system and can be expressed as partial derivatives of various functions. Thus, it follows from Eqs. (1.14)-(1.16) that

$$\mu_i = \left(\frac{\partial U}{\partial m_i}\right)_{S,\, v,\, m_j} = \left(\frac{\partial H}{\partial m_i}\right)_{S,\, p,\, m_j} = \left(\frac{\partial A}{\partial m_i}\right)_{T,\, v,\, m_j} = \left(\frac{\partial G}{\partial m_i}\right)_{T,\, p,\, m_j}, \quad j \neq i \quad (1.17)$$

The chemical potential of a component can therefore be defined as the change in the energy (internal, Helmholtz, Gibbs) of a system caused by a change in the mass of this component by unity at constant masses of the remaining components and at the determining parameters of state (S, v; T, v; or T, p, respectively).

Let us apply Eqs. (1.15) and (1.16) for a chemical reaction. Since $dm_i = \pm \nu_i\, d\lambda$ (+ stands for products and —, for reactants),

the following expression holds:

$$\sum_i \mu_i\, dm_i = \Big(\sum_{i'} \nu_{i'}\mu_{i'}\, d\lambda\Big)_{\mathrm{pr}} - \Big(\sum_i \nu_i\mu_i\, d\lambda\Big)_{\mathrm{r}}$$

$$= \Big(\sum_{i'} \nu_{i'}\mu_{i'} - \sum_i \nu_i\mu_i\Big)\, d\lambda = \sum \nu_i\mu_i\, d\lambda \qquad (1.18)$$

The quantity $\sum \nu_i\mu_i$ stands for the difference of the sums of the products of ν_i and μ_i for the reaction products and reactants. Introducing Eq. (1.18) into (1.15) and (1.16), we find

$$dA = -S\, dT - p\, dv + \sum \nu_i\mu_i\, d\lambda \qquad (1.19a)$$

$$dG = -S\, dT + v\, dp + \sum \nu_i\mu_i\, d\lambda \qquad (1.19b)$$

Many chemical processes are conducted at T, v = const or T, p = = const. It follows from Eqs. (1.19a) and (1.19b) that

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,v} = \left(\frac{\partial G}{\partial \lambda}\right)_{T,p} = \sum \nu_i\mu_i \qquad (1.20)$$

The change in A and G at the expense of a reaction is directly proportional to the amount of reacted substances, i.e. to the change in λ. Therefore,

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,v} = \left(\frac{\Delta A}{\Delta \lambda}\right)_{T,v}, \quad \left(\frac{\partial G}{\partial \lambda}\right)_{T,p} = \left(\frac{\Delta G}{\Delta \lambda}\right)_{T,p}$$

Moreover, if the stoichiometric amounts of the reactants have been used up and the stoichiometric amounts of the products have formed, then $\lambda = \Delta\lambda = 1$. Hence, for changes following the stoichiometric equation ($\Delta\lambda = 1$), the following equations hold:

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,v} = \Delta A = \sum \nu_i\mu_i \qquad (1.21a)$$

$$\left(\frac{\partial G}{\partial \lambda}\right)_{T,p} = \Delta G = \sum \nu_i\mu_i \qquad (1.21b)$$

At equilibrium, A and G are minimal, hence,

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,v} = \left(\frac{\partial G}{\partial \lambda}\right)_{T,p} = 0$$

Therefore, the condition for chemical equilibrium at T, v = const or T, p = const is:

$$\Delta(\nu_i\mu_{i,\mathrm{eq}}) \equiv \sum \nu_i\mu_{i,\mathrm{eq}} = 0 \qquad (1.22)$$

Here $\mu_{i,\mathrm{eq}}$ is the chemical potential of component i in the equilibrium mixture.

The analysis of chemical reactions in multiphase systems is associated with the use of conditions of both chemical and phase equi-

libria. If component i passes over from phase l into phase k, this transition is similar to a chemical process, namely, i in phase $l \rightarrow i$ in phase k.

Accordingly, conditions (1.21) can be written as

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,v} = \mu_i^k - \mu_i^l$$

$$\left(\frac{\partial G}{\partial \lambda}\right)_{T,p} = \mu_i^k - \mu_i^l$$

and since in equilibrium

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,v} = \left(\frac{\partial A}{\partial \lambda}\right)_{T,p} = 0$$

we have

$$\mu_{i,\,eq}^l = \mu_{i,\,eq}^k \tag{1.23}$$

Equation (1.23) determines the conditions of phase equilibrium: at T, v = const or T, p = const, the chemical potentials of each component in all the phases are the same.

Expressions of the Chemical Potential. For the specific use of Eqs. (1.21) and (1.22), we must express the chemical potential as a function of the concentration of a component. Let us consider a mixture of ideal gases for this purpose. The values of A and G for the mixture are determined as the sums of the energies of the components. If the values of the Helmholtz and Gibbs energies per mole of individual component $A_{i,0}$ and $G_{i,0}$ are given for each of the components, then since interaction between the components is absent, we have:

$$A = \sum m_i A_{i,0}, \quad G = \sum m_i G_{i,0}$$

In accordance with Eq. (1.17):

$$\mu_i = \left(\frac{\partial A}{\partial m_i}\right)_{T,v,m_j} = A_{i,0}, \quad \mu_i = \left(\frac{\partial G}{\partial m_i}\right)_{T,p,m_j} = G_{i,0}$$

We know that

$$\left(\frac{\partial A_{i,0}}{\partial v}\right)_T = -p = -\frac{RT}{v}$$

Consequently,

$$\mu_i = A_{i,0} = -RT \ln v + \varphi_i(T)$$

But since v is the volume of one mole of an ideal gas, then by using an equation of state, it can be expressed in terms of the molar concentration c_i, the partial pressure p_i, or the mole fraction x_i of a component:

$$v_i = \frac{1}{c_i} = \frac{RT}{p_i} = \frac{RT}{x_i p}$$

Therefore

$$\mu_i = RT \ln c_i + g_i(T)$$
$$\mu_i = RT \ln p_i + r_i(T)$$
$$\mu_i = RT \ln x_i + h_i(T, p)$$

The arbitrary constants g_i, r_i, and h_i do not depend only on the concentration of component i expressed in terms of c_i (the molar concentration), p_i (the partial pressure), or x_i (the mole fraction); g_i and r_i depend on the temperature, and h_i, on the temperature and pressure. We can separate the part of the expression of μ_i depending on the temperature (g_i, r_i) or on the temperature and pressure (h_i), but not on the concentration. In the following, this part will be designated by $\mu_{i,0}$, i.e. we shall use the equations

$$\mu_i = \mu_{i,10} + RT \ln p_i \tag{1.24a}$$
$$\mu_i = \mu_{i,20} + RT \ln c_i \tag{1.24b}$$
$$\mu_i = \mu_{i,30} + RT \ln x_i \tag{1.24c}$$

It is quite obvious that $\mu_{i,10} = r_i$, $\mu_{i,20} = q_i$, and $\mu_{i,30} = h_i$. The subscripts 1, 2 and 3 on $\mu_{i,0}$ are sometimes omitted. The form of the relation for μ_i shows what $\mu_{i,0}$ depends on.

For a real gas mixture, owing to the absence of a good theory, the dependence of the chemical potential on the composition is expressed by an equation similar to (1.24a) by introducing an effective quantity—the **fugacity** f_i—instead of the partial pressure:

$$\mu_i = \mu_{i,0} + RT \ln f_i \tag{1.25}$$

For an ideal solution, the mole fraction x_i^{lq} of component i in the solution is related to the partial pressure of the component in the equilibrium gas phase and to the saturated vapour pressure p_i° of the pure component by Raoult's law:

$$p_i = p_i^\circ x_i^{lq} \tag{1.26}$$

Moreover, in phase equilibrium, the chemical potentials of a component in the gas (μ_i) and liquid (μ_i^{lq}) phases are the same. Therefore,

$$\mu_i^{lq} = \mu_i = \mu_{i,0} + RT \ln p_i = \mu_{i,0} + RT \ln (p_i^\circ x_i^{lq}) = \mu_{i,40} + RT \ln x_i^{lq} \tag{1.27}$$

Here

$$\mu_{i,40} = \mu_{i,0} + RT \ln p_i^\circ = \psi(T)$$

We shall omit the subscript 4 in the following.

For real liquid and solid solutions, owing to the absence of a good theory, an effective quantity—the **activity** a_i—is introduced instead of x_i^{lq} in the relation showing how the chemical potential depends

on the composition. The expression for the chemical potential of a component of a condensed phase is written in the form

$$\mu_i^{cd} = \mu_{i,0} + RT \ln a_i, \quad \mu_{i,0} = \mu_{i,0}(T, p) \tag{1.28}$$

If the liquid or condensed phase is an individual substance, then $x_i^{lq} = a_i = 1$. In this case, the chemical potential is not related to the concentration and pressure in the system:

$$\mu_i = \mu_{i,0} = \psi(T)$$

1.1.4. Equations Relating the Equilibrium Constant and the Composition of an Equilibrium Mixture (the Law of Mass Action)

The general condition for the equilibrium of chemical reactions proceeding at constant temperature and volume or temperature and pressure, i.e. Eq. (1.22)

$$\sum \nu_i \mu_{i,\text{eq}} = 0$$

holds for any states of the reactants.

Ideal Gas Mixture. If we substitute into Eq. (1.22) the expression for the chemical potential of a component of an ideal equilibrium (subscript "eq") gas mixture (1.24a), we obtain

$$RT \sum \nu_i \ln p_{i,\text{eq}} = -\sum \nu_i \mu_{i,0}$$

or

$$\sum \nu_i \ln p_{i\ \text{eq}} = -\frac{\sum \nu_i \mu_{i,0}}{RT} \equiv -\ln K_p \tag{1.29a}$$

Therefore,

$$K_p = \prod p_{i,\text{eq}}^{\nu_i}, \quad K_p = K_p(T) \tag{1.29b}$$

Similarly, expressing μ_i in terms of the molar concentration $c_{i,\text{eq}}$ or mole fractions $x_{i,\text{eq}}$, we obtain equations for the equilibrium constants K_c and K_x:

$$\sum \nu_i \ln c_{i,\text{eq}} = -\frac{\sum \nu_i \mu_{i,0}}{RT} \equiv \ln K_c \tag{1.30a}$$

$$K_c = \prod c_{i,\text{eq}}^{\nu_i}, \quad K_c = K_c(T) \tag{1.30b}$$

$$\sum \nu_i \ln x_{i,\text{eq}} = -\frac{\sum \nu_i \mu_{i,0}}{RT} \equiv \ln K_x \tag{1.31a}$$

$$K_x = \prod x_{i,\text{eq}}^{\nu_i}, \quad K_x = K_x(T, p) \tag{1.31b}$$

Thus, a reaction in an ideal gas phase can be characterized by the equilibrium constants K_p, K_c, and K_x.

Real Gas Mixture. If the laws of ideal gases are not observed, one should use expression (1.25) for the chemical potential of a real gas. Inserting it into Eq. (1.22), we find

$$\sum \nu_i \ln f_{i,\,\mathrm{eq}} = -\frac{\sum \nu_i \mu_{i,\,0}}{RT} \equiv \ln K_f \tag{1.32a}$$

$$K_f = \prod f_{i,\,\mathrm{eq}}^{\nu_i}, \quad K_f = K_f(T) \tag{1.32b}$$

Thus, a reaction in a real gas mixture is characterized by the equilibrium constant K_f.

Ideal Solution. Introducing into the equilibrium equation (1.22) the expression for the chemical potential of an ideal solution component, we find:

$$\sum \nu_i \ln x_{i,\,\mathrm{eq}}^{\mathrm{lq}} = -\frac{\sum \nu_i \mu_{i,\,0}}{RT} \equiv \ln K_{x^{\mathrm{lq}}} \tag{1.33a}$$

$$K_{x^{\mathrm{lq}}} = \prod x_{i,\,\mathrm{eq}}^{\mathrm{lq},\,\nu_i}, \quad K_{x^{\mathrm{lq}}} = K_{x^{\mathrm{lq}}}(T) \tag{1.33b}$$

For a reaction in an ideal solution, we have

$$x_i^{\mathrm{lq}} = \frac{c_i^{\mathrm{lq}}}{\sum c_i^{\mathrm{lq}}}$$

In an ideal solution (which is a greatly diluted real solution), the sum of the concentrations of all the components is constant, i.e.

$$\sum c_i^{\mathrm{lq}} = \mathrm{const} \equiv b$$

Therefore, equilibrium in an ideal solution is characterized by the constants K_x^{lq} and K_c^{lq}. The latter also depends only on the temperature:

$$K_{c^{\mathrm{lq}}} = K_{x^{\mathrm{lq}}} b^{-\sum \nu_i}, \quad K_{c^{\mathrm{lq}}} = K_{c^{\mathrm{lq}}}(T)$$

Real Solution. Similarly, using the expression for a real solution, we obtain

$$\sum \nu_i \ln a_{i,\,\mathrm{eq}} = -\frac{\sum \nu_i \mu_{i,\,0}}{RT} \equiv \ln K_a \tag{1.34a}$$

$$K_a = \prod a_{i,\,\mathrm{eq}}^{\nu_i}, \quad K_a = K_a(T) \tag{1.34b}$$

Thus, equilibrium in a real solution is characterized by the constant K_a.

Heterogeneous Systems. If the reaction

$$\nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B} \rightarrow \nu_{\mathrm{A}_1}\mathrm{A}_1 + \nu_{\mathrm{B}_1}\mathrm{B}_1 \tag{I}$$

proceeds, where substances A and A_1 are in the gaseous phase, while B and B_1 form independent condensed systems, then for an ideal sys-

tem we have:

$$\mu_{A,\,eq} = \mu_{0,\,A} + RT \ln p_{A,\,eq}, \quad \mu_{A_1,\,eq} = \mu_{0,\,A_1} + RT \ln p_{A_1,\,eq}$$
$$\mu_{B,\,eq} = \mu_{0,\,B}, \quad \mu_{B_1,\,eq} = \mu_{0,\,B_1}$$

Introducing these expressions into the general condition of equilibrium (1.22), we find:

$$-\nu_A RT \ln p_{A,\,eq} + \nu_{A_1} \ln p_{A_1,\,eq}$$
$$= \frac{-\nu_A \mu_{0,\,A} - \nu_B \mu_{0,\,B} + \nu_{A_1} \mu_{0,\,A_1} + \nu_{B_1} \mu_{0,\,B_1}}{RT} = -\frac{\sum \nu_i \mu_{i,\,0}}{RT} \equiv \ln K_p \tag{1.35a}$$

$$K_p = \frac{p_{A_1,\,eq}^{\nu_{A_1}}}{p_{A,\,eq}^{\nu_A}}, \quad K_p = K_p(T) \tag{1.35b}$$

Thus, in this case, the expression for the equilibrium constant K_p includes the partial pressures of only the gaseous components of the reacting mixture.

For a reaction in a non-ideal heterogeneous system when B and B_1 form independent phases, a similar treatment leads to the expressions:

$$-\nu_A \ln f_{A,\,eq} + \nu_{A_1} \ln f_{A_1,\,eq} = -\frac{\sum \nu_i \mu_{i,\,0}}{RT} \equiv \ln K_f \tag{1.36a}$$

$$K_f = \frac{f_{A_1,\,eq}^{\nu_{A_1}}}{f_{A,\,eq}^{\nu_A}}, \quad K_f = K_f(T) \tag{1.36b}$$

If B and B_1 form a liquid or solid solution, then

$$\mu_B = \mu_{0,\,B} + RT \ln a_{B,\,eq}, \quad \mu_{B_1} = \mu_{0,\,B_1} + RT \ln a_{B_1,\,eq}$$

Now the introduction of $\mu_{i,eq}$ into the equilibrium condition ($\sum \nu_i \mu_{i,eq} = 0$) results in the condition

$$-\nu_A \ln f_{A,\,eq} - \nu_B \ln a_{B,\,eq} + \nu_{A_1} \ln f_{A_1,\,eq} + \nu_{B_1} \ln a_{B_1,\,eq}$$
$$= -\frac{\sum \nu_i \mu_{i,\,0}}{RT} \equiv \ln K_{f,\,a} \tag{1.37a}$$

$$K_{f,\,a} = \frac{f_{A_1,\,eq}^{\nu_{A_1}}}{f_{A,\,eq}^{\nu_A}} \frac{a_{B_1,\,eq}^{\nu_{B_1}}}{a_{B,\,eq}^{\nu_B}}, \quad K_{f,\,a} = K_{f,\,a}(T) \tag{1.37b}$$

Hence, a reaction in a real solution is characterized by the equilibrium constants K_f or $K_{f,a}$.

1.1.5. Equations of a Reaction Isotherm, Isochor, and Isobar

The equations of an isotherm are obtained on the basis of Eqs. (1.21). It must be stressed that when obtaining them, integration is performed for the transformation of stoichiometric amounts of the reactants and for the formation of stoichiometric amounts of the products; moreover, it is considered that the amounts of the reactants are so great that the changes in the masses due to the reaction do not change the partial pressures of the components appreciably. Hence, μ_i do not depend on λ, and the following relations hold:

$$\Delta G = \sum \nu_i \mu_i, \quad T,\ p = \text{const}$$

$$\Delta A = \sum \nu_i \mu_i, \quad T,\ v = \text{const}$$

Ideal Gas Mixture. Substituting for μ_i in Eq. (1.21b) its expression from (1.24a) and taking account of Eq. (1.29a) for the equilibrium constant K_p, we obtain for T, p = const:

$$\Delta G = RT\left(\ln \prod p_i^{\nu_i} - \ln K_p\right) \tag{1.38a}$$

Similarly, substituting for μ_i in Eq. (1.21b) its expression from (1.24b) and taking account of Eq. (1.30a) for the equilibrium constant K_c, we obtain for T, v = const:

$$\Delta A = RT\left(\ln \prod c_i^{\nu_i} - \ln K_c\right) \tag{1.38b}$$

Relations (1.38) are called the equations of a reaction isotherm for reactions in an ideal gas mixture.

Real Gas Mixture. For real gases, by substituting for the chemical potential in Eq. (1.21b) its expression from (1.25) and taking account of Eq. (1.32a) for the equilibrium constant K_f, we obtain for T, p = const:

$$\Delta G = RT\left(\ln \prod f_i^{\nu_i} - \ln K_f\right) \tag{1.39}$$

Ideal Solution. From Eqs. (1.21b), (1.27), and (1.33a), we find:

$$\Delta G^{\text{lq}} = RT\left(\ln \prod x_{i,\,\text{lq}}^{\nu_i} - \ln K_{x^{\text{lq}}}\right), \quad T,\ p = \text{const} \tag{1.40a}$$

$$\Delta A^{\text{lq}} = RT\left(\ln \prod x_{i,\,\text{lq}}^{\nu_i} - \ln K_{x^{\text{lq}}}\right), \quad T,\ v = \text{const} \tag{1.40b}$$

Real Solution. By analogy with the above and on the basis of Eqs. (1.21), (1.27), and (1.34a), we obtain:

$$\Delta G^{\text{lq}} = RT\left(\ln \prod a_i^{\nu_i} - \ln K_a\right), \quad T,\ p = \text{const} \tag{1.41a}$$

$$\Delta A^{\text{lq}} = RT\left(\ln \prod a_i^{\nu_i} - \ln K_a\right), \quad T,\ v = \text{const} \tag{1.41b}$$

Heterogeneous Systems. Let us consider reaction (I) (p. 31) and, as previously, we shall assume that B and B_1 form independent

phases. Hence, using the general condition for chemical equilibrium (1.22), the expressions for the chemical potentials of the components, and Eq. (1.35a) for the equilibrium constant K_p, we obtain for T, p = const:

$$\Delta G = RT\left(\ln \frac{p_{A_1}^{\nu_{A_1}}}{p_A^{\nu_A}} - \ln K_p\right) \tag{1.42}$$

Similarly, for a reaction in a non-ideal heterogeneous system (B and B_1 form independent phases as previously), by combining Eqs. (1.22), (1.28), and (1.36), we have for T, p = const:

$$\Delta G = RT\left(\ln \frac{f_{A_1}^{\nu_{A_1}}}{f_A^{\nu_A}} - \ln K_f\right) \tag{1.43}$$

If B and B_1 form a liquid or solid solution, then on the basis of Eqs. (1.22), (1.28), and (1.36), we find for T, p = const:

$$\Delta G = RT\left(\ln \frac{f_{A_1}^{\nu_{A_1}}}{f_A^{\nu_A}} \cdot \frac{a_{B_1}^{\nu_{B_1}}}{a_B^{\nu_B}} - \ln K_{f,a}\right) \tag{1.44}$$

Consequently, we can calculate the equilibrium constant of a reaction proceeding in any reaction system from the value of ΔG or ΔA and the composition of the initial mixture.

Table 2 presents the fundamental relations following from the second law of thermodynamics.

By differentiating the equation of an isotherm with respect to the temperature and using the indicated relations, we can obtain the temperature dependence of the equilibrium constant, namely, the equation of an isobar or isochor.

For example, for an ideal gas mixture, Eqs. (1.38a) and (1.38b) are observed. Differentiating with respect to T (the pressure or volume is constant), we have:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \frac{\Delta G}{T} - RT\left(\frac{\partial \ln K_p}{\partial T}\right)_p$$

$$\left(\frac{\partial \Delta A}{\partial T}\right)_v = \frac{\Delta A}{T} - RT\left(\frac{\partial \ln K_c}{\partial T}\right)_v$$

But we know that

$$\left(\frac{\partial G}{\partial T}\right)_p = \left(\frac{\partial A}{\partial T}\right)_v = -S, \qquad \left(\frac{\partial \Delta G}{\partial T}\right)_p = \left(\frac{\partial \Delta A}{\partial T}\right)_v = -\Delta S$$

Also having in view that $\Delta G = \Delta H - T\Delta S$ and $\Delta A = \Delta U - T\Delta S$, we find:

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H}{RT^2} \quad \text{(equation of an isobar)}$$

$$\left(\frac{\partial \ln K_c}{\partial T}\right)_v = \frac{\Delta U}{RT} \quad \text{(equation of an isochor)}$$

Table 2. **Fundamental Relations Following from the Second Law of Thermodynamics for a Complex Thermodynamic System in Which the Masses of the Components Change**

Name	Relation
Second law of thermodynamics:	
General form	$dS \geqslant \delta Q/T,\ T\,dS = \delta Q + \delta Q',\ \delta Q' \geqslant 0$
$T,\ v = \text{const}$	$\delta Q' = -dA,\ A = U - TS$
$T,\ p = \text{const}$	$\delta Q' = -dG,\ G = H - TS$
General conditions of equilibrium:	
Isolated system	$dS = 0$, the entropy S is maximum
$T,\ v = \text{const}$	$dA = 0$, the Helmholtz energy A is minimum
$T,\ p = \text{const}$	$dG = 0$, the Gibbs energy G is minimum
Relations for the derivatives of A and G	$\left(\frac{\partial A}{\partial T}\right)_{v, m_i} = -S,\ \left(\frac{\partial A}{\partial v}\right)_{T,\ m_i} = -p$ $\left(\frac{\partial G}{\partial T}\right)_{p,\ m_i} = -S,\ \left(\frac{\partial G}{\partial p}\right)_{T,\ m_i} = v$
Determination of the chemical potential	$\mu_i = \left(\frac{\partial U}{\partial m_i}\right)_{v,\ S,\ m_j} = \left(\frac{\partial A}{\partial m_i}\right)_{T,\ v,\ m_j}$ $= \left(\frac{\partial G}{\partial m_i}\right)_{T,\ p,\ m_j}$
Conditions for chemical equilibrium:	
$T,\ v = \text{const}$ $T,\ p = \text{const}$	$\Delta(\nu_i \mu_i, \text{eq}) \equiv \sum \nu_i \mu_{i,\ \text{eq}} = 0$
Corollaries of the second law of thermodynamics:	
Equation for the chemical potential:	
ideal gas	$\mu_i = \mu_{i,\ 0}(T) + RT \ln c_i = \mu_{i,\ 10}(T) + RT \ln p_i$ $= \mu_{i,\ 20}(T) + RT \ln x_i$
real gas	$\mu_i = \mu_{i,\ 0}(T) + RT \ln f_i$
Equation of an isotherm for a reaction in an ideal gas mixture:	
$T,\ v = \text{const}$	$\Delta A = RT \left\{ \ln \frac{c_{10}'^{\nu_1'} c_{20}'^{\nu_2'} \cdots}{c_{10}^{\nu_1} c_{20}^{\nu_2} \cdots} - \ln K_c \right\}$
$T,\ p = \text{const}$	$\Delta G = RT \left\{ \ln \frac{p_{10}'^{\nu_1'} p_{20}'^{\nu_2'} \cdots}{p_{10}^{\nu_1} p_{20}^{\nu_2} \cdots} - \ln K_p \right\}$ $\Delta G^\circ = -RT \ln K_p^\circ$

Table 2 (*concluded*)

Name	Relation
Temperature dependence of equilibrium constants:	
$p = \text{const}$	$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H}{RT^2}$
$v = \text{const}$	$\left(\frac{\partial \ln K_c}{\partial T}\right)_v = \frac{\Delta U}{RT^2}$
Equation of an isotherm for a reaction in a real gas mixture:	
$T,\ p = \text{const}$	$\Delta G = RT\left\{\ln \frac{f_{10}'^{\nu_1'} f_{20}'^{\nu_2'} \cdots}{f_{10}^{\nu_1} f_{20}^{\nu_2} \cdots} - \ln K_f\right\}$ $\Delta G^\circ = -RT \ln K^\circ f$

1.1.6. Differential Relations of Thermodynamics

The calculations of ΔU, ΔH, ΔS, ΔA, and ΔG for chemical reactions at arbitrary values of v, p, and T require the determination of the partial derivatives of U, H, S, A, and G of the individual substances with respect to v, p, and T. These derivatives (they are called the differential relations of thermodynamics) are obtained from different forms of the equations of the first and second laws for an equilibrium ($\delta Q' = 0$) and simple thermodynamic system. The independence of the second mixed derivative of the order of differentiation is used additionally. For example, for a simple thermodynamic system from the first law ($\delta Q = dU + p\,dv = C_v\,dT + h_v dv$), we have

$$dU = C_v\,dT + (h_v - p)\,dv \tag{1.45a}$$

From the second law, we find

$$dS = \frac{\delta Q}{T} = \frac{C_v}{T}\,dT + \frac{h_v}{T}\,dv \tag{1.45b}$$

Since the second mixed derivative is independent of the order of differentiation, we obtain from Eq. (1.45a) that

$$\left(\frac{\partial C_v}{\partial v}\right)_T = \left(\frac{\partial h_v}{\partial T}\right)_v - \left(\frac{\partial p}{\partial T}\right)_v \tag{1.45c}$$

It follows from Eq. (1.45b) that

$$\left[\frac{\partial (C_v/T)}{\partial v}\right] = \left[\frac{\partial (h_v/T)}{\partial T}\right]_v$$

or

$$\left(\frac{\partial C_v}{\partial T}\right)_v = \left(\frac{\partial h_v}{\partial T}\right)_v - \frac{h_v}{T} \tag{1.45d}$$

By equating the right-hand sides of Eqs. (1.45c) and (1.45d), we obtain the Clausius-Clapeyron equation

$$h_v = T\left(\frac{\partial p}{\partial T}\right)_v. \tag{1.46a}$$

Similarly, we find

$$h_p = -T\left(\frac{\partial v}{\partial T}\right)_p \tag{1.46b}$$

Let us now see how the internal energy U depends on the temperature T and volume v. From Eqs. (1.45a) and (1.46a), we have

$$\left(\frac{\partial U}{\partial T}\right)_v = C_v, \quad \left(\frac{\partial U}{\partial v}\right)_T = h_v - p = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

We can find the derivatives of the other thermodynamic functions in a similar way. The most important differential relations of thermodynamics are given below.

Heat capacity:

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v, \quad \left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$$

Internal energy:

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p, \quad \left(\frac{\partial U}{\partial T}\right)_v = C_v$$

$$\left(\frac{\partial U}{\partial p}\right)_v = C_v\left(\frac{\partial T}{\partial p}\right)_v$$

$$\left(\frac{\partial U}{\partial v}\right)_p = C_p\left(\frac{\partial T}{\partial v}\right)_p - p, \quad \left(\frac{\partial U}{\partial T}\right)_p = C_p - p\left(\frac{\partial v}{\partial T}\right)_p$$

$$\left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T$$

Enthalpy:

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p + v, \quad \left(\frac{\partial H}{\partial T}\right)_p = C_p, \quad \left(\frac{\partial H}{\partial v}\right)_p = C_p\left(\frac{\partial T}{\partial v}\right)_p$$

$$\left(\frac{\partial H}{\partial p}\right)_v = C_v\left(\frac{\partial T}{\partial p}\right)_v + v, \quad \left(\frac{\partial H}{\partial p}\right)_v = C_p\left(\frac{\partial T}{\partial p}\right)_v + v - T\left(\frac{\partial v}{\partial T}\right)_p$$

$$\left(\frac{\partial H}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v + v\left(\frac{\partial p}{\partial v}\right)_T$$

Entropy:

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T}, \quad \left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v, \quad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

$$\left(\frac{\partial S}{\partial p}\right)_v = \frac{C}{T}\left(\frac{\partial T}{\partial p}\right)_v, \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p, \quad \left(\frac{\partial S}{\partial v}\right)_p = \frac{C}{T}\left(\frac{\partial T}{\partial v}\right)_p$$

Helmholtz energy:

$$\left(\frac{\partial A}{\partial T}\right)_v = -S, \quad \left(\frac{\partial A}{\partial v}\right)_T = -p$$

Gibbs energy:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \quad \left(\frac{\partial G}{\partial p}\right)_T = v$$

For calculations employing the differential relations of thermodynamics, one must use the equation of state of a substance $\varphi = (T, p, v) = 0$.

This equation is the simplest for an ideal gas. For one mole, we have $pv = RT$, and the above equations acquire the following forms:

Heat capacity:

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T \cdot 0 = 0, \quad \text{i.e. } C_v = C_v(T)$$

$$\left(\frac{\partial C}{\partial p}\right)_T = -T \cdot 0 = 0, \quad \text{i.e } C_p = C_p(T)$$

$$C_p - C_v = T\frac{R}{v} \cdot \frac{R}{p} = R$$

Internal energy:

$$\left(\frac{\partial U}{\partial v}\right)_T = T\frac{R}{v} - p = 0, \quad \text{i.e. } U = U(T)$$

$$\left(\frac{\partial U}{\partial T}\right)_v = \frac{dU}{dT} = C_v, \quad \text{i.e. } \Delta U = C_v \Delta T$$

Enthalpy:

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\frac{R}{p} + v = 0, \quad \text{i.e. } H = H(T)$$

$$\left(\frac{\partial H}{\partial T}\right)_p = \frac{dH}{dT} = C_p, \quad \text{i.e. } \Delta H = C_p \Delta T$$

Entropy:

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T}, \quad \text{i.e. } \Delta S = C_v \ln \frac{T}{T_1}$$

$$\left(\frac{\partial S}{\partial v}\right)_T = \frac{R}{v} dv, \quad \text{i.e. } \Delta S = R \ln \frac{v}{v_1} = R \ln \frac{p_1}{p}$$

Helmholtz energy:

$$dA = -p\,dv = -\frac{RT}{v} dv, \quad A = -RT \ln v + \varphi(T)$$

Gibbs energy:

$$dG = v\,dp = \frac{RT}{p} dp, \quad G = RT \ln p + \psi(T)$$

Similar calculations are performed for real gases and liquids by using semi-empirical equations of state.

1.2. Equations of State of a Real Gas (Liquid)

To calculate the thermodynamic functions of substances with the aid of the differential relations of thermodynamics, we use equations of state containing a different number of parameters (constants).

At the critical point (i.e. at $T = T_{cr}$, $p = p_{cr}$, and $v = v_{cr}$), for any real gas, we have

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$$

These conditions enable us to obtain useful relations between the parameters of an equation of state and T_{cr}, p_{cr}, and v_{cr}.

The van der Waals equation contains two parameters (a and b). Its form for one mole of a gas is:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{1.47}$$

It follows from Eq. (1.47) that

$$a = \frac{27}{64}\frac{R^2T_{cr}^2}{p_{cr}}, \qquad b = \frac{RT_{cr}}{8p_{cr}} = \frac{v_{cr}}{3}, \qquad Z_{cr} = \frac{pv_{cr}}{RT_{cr}} = \frac{3}{8}$$

(Here Z is the compression factor.) If we go over to the reduced parameters $\tau = T/T_{cr}$, $\pi = p/p_{cr}$, and $\varphi = v/v_{cr}$ in Eq. (1.47), we obtain

$$\left(\pi + \frac{3}{\varphi^2}\right)(3\varphi - 1) = 8\tau \tag{1.48}$$

The van der Waals equation, like Eq. (1.48), yields good results only for low pressures and does not greatly improve calculations in comparison with the equation for an ideal gas.

However, the law of corresponding states, according to which for any gases at identical values of τ and π the values of φ, Z, etc. coincide, was found to hold for real systems and has found widespread use [5, 6]. Particularly, we can state on the basis of this principle that if the equation of state for one mole of a real gas is written by introducing the compression factor Z, namely:

$$pv = ZRT \quad \text{or} \quad \pi\varphi = \frac{Z}{Z_{cr}}\tau$$

where

$$Z = \frac{p_{cr}v_{cr}}{RT_{cr}} \tag{1.49}$$

then Z is determined for a gas by any pair of the reduced parameters, for example, τ and π (Fig. 1).

The Redlich-Quong equation is considered to be the best of the ones containing two parameters:

$$p = \frac{RT}{v - b_p} - \frac{a_p}{T^{1/2}v(v + b_p)} \tag{1.50}$$

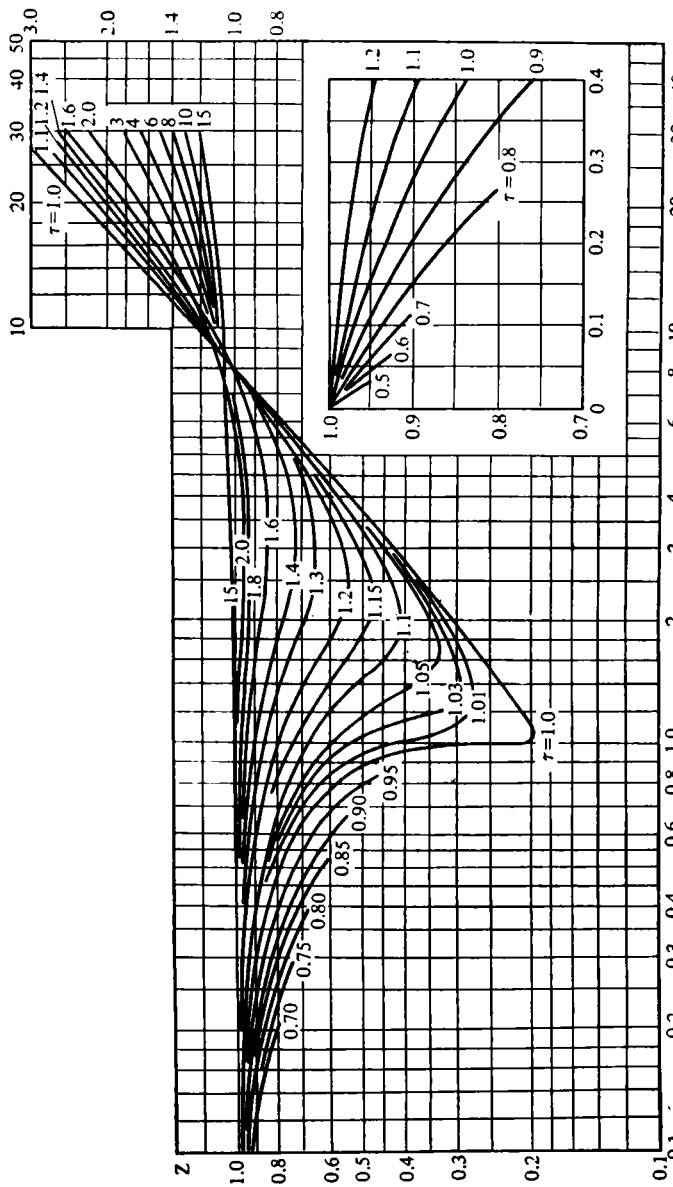


Fig. 1. Compression factor Z as a function of the reduced parameters τ and π at $Z_{cr} = 0.27$

It follows from the above conditions for the critical point that

$$a_p = \frac{0.427\,48 R^2 T_{cr}^{5/2}}{p_{cr}}, \quad b_p = \frac{0.086\,64 R T_{cr}}{p_{cr}}$$

Multiparametric Equations. The Beattie-Bridgman equation contains five parameters (A_0, a, B_0, b and C), and for one mole of a gas has the form

$$pv^2 = RT\left[v + B_0\left(1 - \frac{b}{v}\right)\right]\left(1 - \frac{C}{vT^3}\right) - A_0\left(1 - \frac{a}{v}\right) \qquad (1.51)$$

The Benedict-Webb-Rubin equation contains eight parameters (A_0, a, B_0, b, C_0, c, α, and γ), and for one mole of a gas has the form

$$p = \frac{RT}{v} + \frac{1}{v^2}\left(RTB_0 - A_0 - \frac{C_0}{T^2}\right) + \frac{1}{v^3}(RTb - a)$$
$$+ \frac{a\alpha}{v^6} + \frac{c}{T^2 v^3}\left(1 + \frac{\gamma}{v^2}\right)\exp\left(-\frac{\gamma}{v^2}\right) \qquad (1.52)$$

Equations (1.51) and (1.52) can be used within a broad range of temperatures and pressures.

A virial equation (for one mole of a gas) is written in the form

$$pv = RT + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \ldots$$

or

$$pv = RT + B'(T)\,p + C'(T)\,p^2 + D'(T)\,p^3 + \ldots \qquad (1.53)$$

Gas Mixtures. The equations of state for a gas mixture can be obtained on the basis of Dalton's law (the equality of the sum of the partial pressures p_i to the pressure p), namely, $\sum p_i = p$, or of Amagat's law (the equality of the sum of the partial volumes v_i to the volume of the mixture v), namely, $\sum v_i = v$.

For a mixture of ideal gases, Dalton's law yields

$$p = \sum p_i = \frac{\sum m_i RT}{v} \quad \text{or} \quad pv = \sum m_i RT$$

For a mixture of real gases, we have to use an empirical equation of state with the compression factor Z_m

$$pv = Z_m \sum m_i RT$$

If Dalton's law holds, we have

$$Z_m = \frac{v}{\sum m_i RT}\sum p_i = \sum \frac{m_i}{\sum m_i}\cdot\frac{pv}{m_i RT} = \sum x_i Z_i \qquad (1.54)$$

where $x_i = m_i/\sum m_i$, and $Z_i = p_i v/m_i RT$ is the compression factor of component i.

Other semi-empirical relations similar to (1.54) are used for calculating the critical temperature and pressure of a mixture $T_{m,cr}$ and $p_{m,cr}$:

$$T_{m,cr} = \sum x_i T_{i,cr}, \quad p_{m,cr} = \sum x_i p_{i,cr}$$

The values of $T_{m,cr}$ and $p_{m,cr}$ can be employed to calculate the reduced parameters for a mixture:

$$\tau_m = \frac{T}{T_{m,cr}}, \quad \pi_m = \frac{p}{p_{m,cr}}$$

Now the compression factor can be found by considering the mixture to be a "pseudocomponent" at τ_m and π_m. This approach yields sufficiently accurate values of Z_m, but one must understand that the quantities $T_{m,cr}$ and $p_{m,cr}$ are deprived of a physical meaning.

Semi-empirical equations of state are preferred in the calculation of chemical reactions of real gases. For an individual gas, the equation

$$pv = ZRT \quad \left(\text{or } \pi\varphi = \frac{Z}{Z_{cr}}\tau\right)$$

is used, and for a mixture of gases,

$$pv = Z_m \sum m_i RT \quad \left(\text{or } \pi_m\varphi_m = \frac{Z_m}{Z_{m,cr}}\tau_m\right)$$

The main difficulty when using an equation of the type of $pv = ZRT$ is associated with the involved nature of determining the effective quantity—the compression factor Z. It has been noted above that the value of Z depends on τ and π, namely, $Z = Z(\tau, \pi)$. It follows from this relation that at the critical point ($\tau = 1$ and $\pi = 1$) the compression factor Z_{cr} must be the same for all gases.

But the value of Z_{cr} can be determined from the measured critical parameters, i.e. $Z_{cr} = p_{cr}v_{cr}/RT_{cr}$. It was found that Z_{cr} varies for different substances from 0.2 to 0.3, more exactly from 0.23 to 0.29. It follows from this observation that a relation taking into account the influence of not only τ and π, but also of Z_{cr} on Z, i.e.

$$Z = Z(\tau, \pi, Z_{cr})$$

will be the most universal (correct for all real substances).

It is difficult to establish the form of this relation, while tabulation or graphical interpretation would require a large volume of a book because it is necessary to give tables (or graphs) of $Z = Z(\tau, \pi)$ for $Z_{cr} = 0.20$, 0.205, and so on. However, it was found possible to reduce the volume of such tables or graphs.

Hougen *et al* [3] noted that substances can be classified according to their values of Z_{cr}. This classification includes the following four groups:

Representative substances	Z_{cr}
Water	0.23
Acetone, ammonia, ethers, esters, alcohols	0.24-0.26
Most hydrocarbons, 60% of all organic compounds	0.26-0.28
Oxygen, nitrogen, hydrogen sulphide, carbon monoxide, methane, ethane, noble gases	0.28-0.30

This classification enables us to retain a simple equation for the relation $Z = Z(\tau, \pi)$, which should be used in four different modifications, namely, for $Z_{cr} = 0.23$ (the first group), for $Z_{cr} = 0.25$ (the second group), for $Z_{cr} = 0.27$ (the third group), and for $Z_{cr} = 0.29$ (the fourth group).

Since in this case too tables or graphs have to be compiled for each group of substances to determine Z, and also the fugacity (activity) coefficient, heat capacity, entropy, and enthalpy at increased pressures, which depend on Z, the volume of the reference data needed for calculations still remains quite large. This is why tables or graphs are usually given for the most widespread group of substances ($Z_{cr} = 0.27$) (see Fig. 1). A number of empirical procedures has been proposed for going over from the values of Z, γ, C_p^p, S^p, and ΔH^p found from these tables or graphs to similar quantities for other values of Z_{cr} (0.23, 0.25, and 0.29) [3, 6].

Calculation of Fugacity Coefficient for a Real Gas. It should be noted that the fugacity is a calculated quantity and replaces the pressure in the equation of the chemical potential μ. By definition, for an individual substance, the chemical potential equals the Gibbs energy G of one mole of a substance. If the temperature is constant, then as follows from the relations given in Table 2, for one mole of a real gas we have

$$\left(\frac{\partial G}{\partial p}\right)_T = \left(\frac{\partial \mu}{\partial p}\right)_T = v \quad \text{or} \quad dG = d\mu = v\,dp$$

where v is the volume of one mole of a real gas.

If we use the last equation for an ideal gas ($v_{id} = RT/p$), we obtain

$$d\mu_{id} = RT\,d\ln p$$

By substituting the fugacity for the pressure, we again obtain an equation holding for a real gas:

$$d\mu = RT\,d\ln f$$

Thus, for a real gas $v\,dp = RT\,d\ln f$ or, since we have considered an isothermal process:

$$\left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{v}{RT} \tag{1.55}$$

This equation relates the fugacity to the parameters of state being measured (p, v, T). To obtain a working relation, let us integrate

Eq. (1.55). To do this, we shall use an auxiliary condition:

$$v - v_{\text{id}} - \alpha = \frac{RT}{p} - \alpha \tag{1.56}$$

where α is the difference between the molar volumes of an ideal and real gas. Introducing (1.56) into (1.55), we find:

$$d \ln f = d \ln p - \frac{\alpha}{RT} dp$$

Integration within the limits of f_1 to f for the fugacity and of p_1 to p for the pressure yields

$$\ln f - \ln f_1 = \ln p - \ln p_1 - \frac{1}{RT} \int_{p_1}^{p} \alpha \, dp$$

Let us now take into consideration that at low pressures ($p \to 0$) the properties of a real and ideal gases coincide ($f_1 = p_1$ and $\ln f_1 = \ln p_1$). Hence, we finally obtain

$$\ln \gamma^\circ = \ln \frac{f}{p} = -\frac{1}{RT} \int_{0}^{p} \alpha \, dp \tag{1.57}$$

Equation (1.57) underlies the most developed method of calculating the fugacity (activity) coefficient γ° (what is known as the Newton-Dodge method). It is taken into account that the values of α for various real gases will be close if the corresponding states coincide for these gases (i.e. the values of τ and π). More accurate calculations have shown that for exact coincidence of the values of α for various real gases, it is essential that the values of τ, π, and $Z_{\text{cr}} = p_{\text{cr}} v_{\text{cr}} / RT_{\text{cr}}$ be the same for them, i.e. that the relation $\alpha = \alpha\ (\tau, \pi, Z_{\text{cr}})$ be universal. It has also been established that for hydrogen, helium, and neon, the empirical conditions $\tau = T/(T_{\text{cr}} + 8)$ and $\pi = p/(p_{\text{cr}} + 0.8)$ (where p is the pressure measured in MPa) should be used. Now, having calculated γ° by formula (1.57) for various states (T, p) of a "representative" gas (or saturated vapour pressure of a liquid) and presented the relation $\gamma^\circ = \gamma^\circ\ (\tau, \pi, Z_{\text{cr}})$ in the form of tables or graphs from the results of the calculations, we can use them for any other gases. The results of such calculations performed by Hougen *et al* [3] are given in Figs. 2-6. By using these figures, given respectively for $Z_{\text{cr}} = 0.23$, 0.25, 0.27 ($0 \leqslant \pi \leqslant 3$), 0.27 ($0 \leqslant \pi \leqslant 30$), and $Z_{\text{cr}} = 0.29$, it is not difficult for us to determine γ° for any gas and for any state (T, p, or τ, π) at the known critical parameters (T_{cr}, p_{cr}).

Fugacity of a Component in a Mixture. If the partial pressure of the i-th component of an ideal gas mixture has changed from $p_{i,1}$ to $p_{i,2}$ at a constant temperature, the change in the chemical poten-

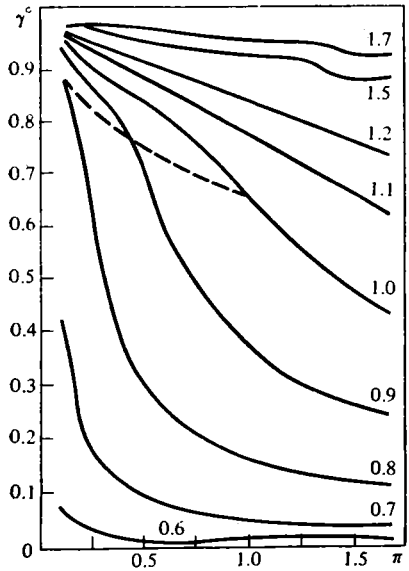


Fig. 2. Fugacity coefficient γ° of an individual substance versus the reduced parameters τ and π for $Z_{cr}=0.23$ (in Figs. 2-6, the numbers on the curves are the values of τ)

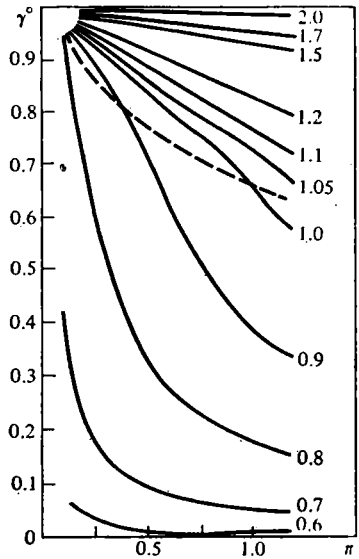


Fig. 3. Fugacity coefficient γ° of an individual substance versus the reduced parameters τ and π for $Z_{cr}=0.25$

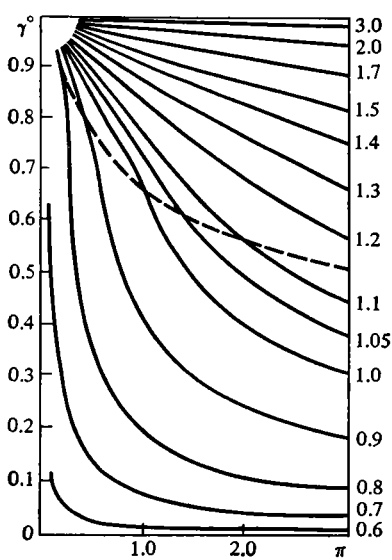


Fig. 4. Fugacity coefficient γ° of an individual substance versus the reduced parameters τ and π for $Z_{cr} = 0.27$, $0 \leqslant \pi \leqslant 3$

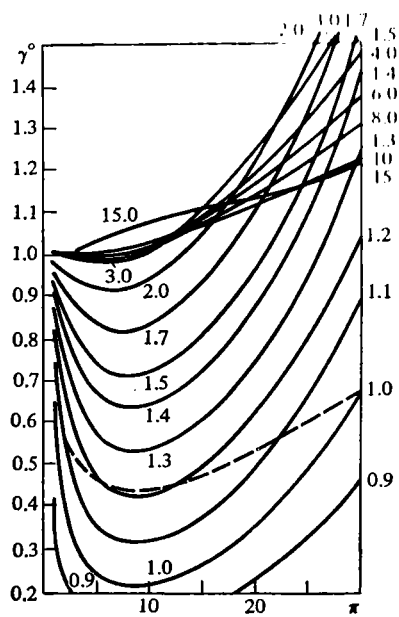


Fig. 5. Fugacity coefficient γ° of an individual substance versus the reduced parameters τ and π for $Z_{cr} = 0.27$, $0 \leqslant \pi \leqslant 30$

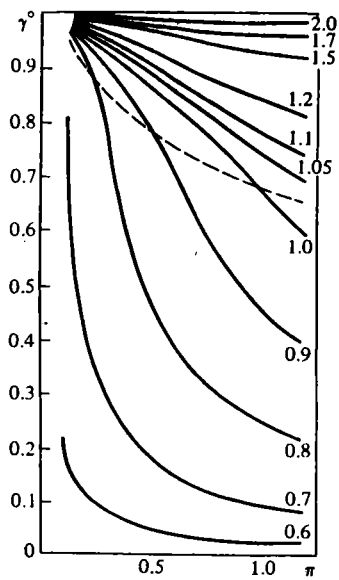


Fig. 6. Fugacity coefficient γ° of an individual substance versus the reduced parameters τ and π for $Z_{cr}=0.29$

tial will be

$$\Delta\mu_i = RT \ln \left(\frac{p_{i,2}}{p_{i,1}}\right)$$

For a real gas mixture, by (1.25):

$$\Delta\mu_i = RT\,(\ln f_{i,2} - \ln f_{i,1}), \quad T = \text{const}$$

or

$$d\mu_i = RT\, d \ln f_i, \quad T = \text{const}$$

Since $d\mu_i = v_i\, dp$, we find from the last two equations that

$$\left(\frac{\partial \ln f_i}{\partial p}\right)_T = \frac{v_i}{RT} \qquad (1.58)$$

Equation (1.58) is formally similar to the fundamental equation for calculating the fugacity of an individual gas (1.55), but requires for calculations that the partial molar volume v_i of a component be determined instead of the molar volume of the pure component v.

At a low total pressure p^*, when the mixture can be considered as ideal, we have

$$f_i^* = p_i^* = x_i p^* \qquad (1.59)$$

Integrating (1.58) from p^* to p with a view to condition (1.59), we obtain:

$$RT \ln f_i = \int_{p^*}^{p} v_i\, dp + RT \ln (x_i p^*) \qquad (1.60)$$

We shall take into account that

$$RT \int_{p^*}^{p} \frac{dp}{p} = RT \ln p - RT \ln p^* \qquad (1.61)$$

Substitution of $RT \ln p^*$ from (1.61) into (1.60) yields

$$RT \ln f_i = \int_{p^*}^{p} \left(v_i - \frac{RT}{p}\right) dp + RT \ln x_i p \qquad (1.62)$$

Equation (1.62) can be used for calculations if the relation $v_i = v_i\,(p)$ at a constant temperature and mixture composition has been

established. Usually the following simplification is resorted to, however.

For a pure component, $x_i = 1$, $f_i = f$, and $v_i = v$, therefore Eq. (1.62) can be written in the form obtained previously for an individual substance:

$$RT \ln f = \int_{p^*}^{p} \left(v - \frac{RT}{p}\right) dp + RT \ln p$$

It also follows from (1.62) that

$$RT \ln f_i = \int_{p^*}^{p} (v_i - v)\, dp + RT \ln x_i f$$

If we introduce the condition

$$f_i = \gamma_i x_i f \tag{1.63}$$

where γ_i is the fugacity (activity) coefficient of the i-th component in the mixture, then by inserting (1.63) into (1.62), we obtain an expression for calculating γ_i:

$$\ln \gamma_i = \frac{1}{RT} \int_{p^*}^{p} (v_i - v)\, dp \tag{1.64}$$

The quantities v_i, v, and then γ_i are generally calculated by equations of state of a real gas and a real gas mixture. Such calculations are described, for example, in [7].

If $v_i = v$ (an ideal solution or ideal gas mixture), it can be easily seen from Eqs. (1.62) and (1.64) that $\gamma_i = 1$ and $f_i = x_i f$. For this case, having in view that $f = \gamma_i^\circ p$, we obtain the approximate condition

$$f_i = x_i \gamma_i^\circ p \tag{1.65}$$

This condition is customarily employed in calculations of chemical equilibria up to pressures of about 10 MPa.

1.3. The Standard State. Standard Thermodynamic Functions

One of the main tasks of chemical thermodynamics is the calculation of the change in the thermodynamic functions in chemical reactions. These calculations are performed using the values of the thermodynamic functions of the reactants given in thermodynamic tables. Such tables cannot be compiled for all possible states of a substance. Consequently, the task arises of choosing a state of substances such that their thermodynamic functions in this state could be

readily determined and used for subsequent thermodynamic calculations.

At present, thermodynamic data are given for the following standard states of substances.

For gases—the state of an ideal gas at standard pressure (101 325 Pa or 1 atm); sometimes, the state of a real gas at standard pressure.

For liquids—the state of a real liquid at standard pressure; sometimes the thermodynamic properties of the hypothetic vapour of the liquid are given for the state of an ideal gas and at standard pressure.

For solids at 298 K—the solid state at 101 325 Pa. If a solid can exist in several modifications at 298 K, the standard state is determined for the thermodynamically stable modification. For example, at 298 K, graphite is the thermodynamically stable state of carbon, and it is taken as its standard state.

For solutions—the state of an ideal solution with a molality equal to unity (one mole of solute per 1000 g of solvent).

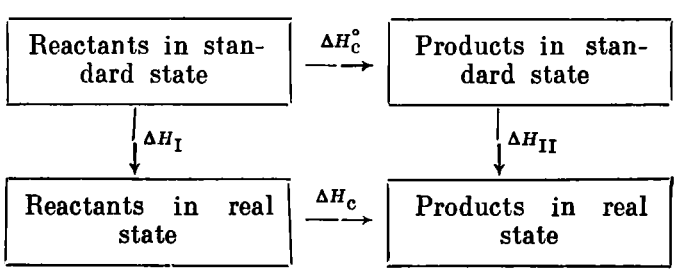
Thus, a state in the form of an ideal gas, liquid, or solid at any temperature, but at a pressure of 101 325 Pa, can be considered as the standard one, it being necessary to indicate the phase state.

Data on the standard thermodynamic functions of benzene at 298 K both in the gaseous and in the liquid state can be found in tables.

The thermodynamic functions of substances in the standard state are called standard and are designated by the superscript °, namely, ΔH°, S°, C_p°, ΔG°, and ΔA°. They are given in standard thermodynamic tables.

By a standard change in a thermodynamic function is meant its change as a result of a chemical reaction when the reactants and products are in the standard state. Naturally, such a process cannot be carried on in a real experiment, and the real pressures have to be converted to the standard one.

For example, the standard heat of combustion ΔH_c° can be calculated from the value of ΔH_c on the basis of the following isothermal cycle:



It is obvious that

$$\Delta H_c^\circ = \Delta H_{\mathrm{I}} + \Delta H_{\mathrm{II}} + \Delta H_c$$

The values of ΔH_{I} and ΔH_{II} are calculated on the basis of the general relations (see Sec. 1.1.6). It can be noted, however, that the value of $(\Delta H_{\mathrm{I}} + \Delta H_{\mathrm{II}})$ is small in comparison with ΔH_c°. Thus, for the combustion of one mole of naphthalene, $\Delta H_c^\circ = -5156.8$ kJ/mol, while $\Delta H_{\mathrm{I}} + \Delta H_{\mathrm{II}} = 3.6$ kJ/mol.

As regards ΔH_f° and ΔG_f°, these quantities are calculated from the standard heats of combustion and the entropies of simple substances and compounds.

Thermodynamic calculations are performed with the aid of tables of the standard thermodynamic functions. Such tables are given in Appendix 2 for simple substances and compounds (the latter in the state of an ideal gas at 101 325 Pa) most frequently encountered in thermodynamic calculations for petroleum refining and petrochemistry.

The use of such tables sometimes requires the ability of converting the functions given in them for the state of an ideal gas to the state of a substance in which it participates in a physicochemical process. In essence, one has to return to the calculations that were performed when compiling the tables, but cannot be given in them because of space limitations. Conversion is performed with the aid of the relations given in Table 3 that follow from the first and second laws of thermodynamics for one mole of a substance.

How calculations are performed using these relations is illustrated below. Various semi-empirical techniques are used in the calculations for determining the form and values of the derivatives $(\partial v/\partial T)_p$ and $(\partial^2 v/\partial T^2)_p$, and also of Δv, ΔH_v, and ΔH_{sub}.

1.4. Calculations of Heat Capacities

The temperature dependence of the heat capacity is written in the form of the empirical polynomial equation

$$C_p = a + bT + cT^2 + dT^{-2}$$

or of its simplified forms with $d = 0$ or $d = c = 0$.

The coefficients a, b, c, and d are determined from the experimentally measured values of the heat capacity C_p^{ex} at various temperatures, but at a constant pressure. The method of least squares is used for this purpose. In this method, the coefficients are chosen by minimizing the sum of the squares of the deviations between the calculated (C_p) and experimental (C_p^{ex}) values:

$$F = \sum_k (C_{p,k} - C_{p,k}^{\mathrm{ex}})^2 = \sum_k (a + bT_k + cT_k^2 + dT_k^{-2} - C_{p,k}^{\mathrm{ex}})^2 \to \min$$

where k is the number of the measured and calculated value.

A system of algebraic equations for determining the coefficients

Table 3. **Relations for Calculating the Thermodynamic Functions**

Ideal gas		Real gas	Liquid	Solid
at standard pressure	at pressure p	at pressure p	at standard pressure	
C_p°	$C_p = C_p^\circ$	$C_p = C_p^\circ - \int_0^p \left[T\left(\frac{\partial^2 v}{\partial T^2}\right)\right] dp$	$C_{lq}^\circ \neq \varphi(C_p^\circ)$	$C_s^\circ \neq \varphi(C_p^\circ)$
S°	$S = S^\circ - R\ln\frac{p}{p^\circ}$	$S = S^\circ - \int_0^p \left(\frac{\partial v}{\partial T}\right)_p dp$	$S_{lq}^\circ = S^\circ - \int_0^{p_0} \left(\frac{\partial v}{\partial T}\right)_p dp - \frac{\Delta H_v}{T}$	$S_s^\circ = S^\circ - \int_0^{p^0} \left(\frac{\partial v}{\partial T}\right)_p dp - \frac{\Delta H_{sub}}{T}$
ΔH_f°	$\Delta H_f = \Delta H_f^\circ$	$\Delta H_f = \Delta H_f^\circ - \int_0^p \left[T\left(\frac{\partial \Delta v_f}{\partial T}\right)_p + \Delta v_f\right] dp$	$\Delta H_{f,\,lq}^\circ \approx \Delta H_f^\circ - \Delta H_v^\circ$	$\Delta H_{f,\,s}^\circ \approx \Delta H_f^\circ - \Delta H_{sub}^\circ$
ΔG_f°	$\Delta G_f = \Delta G_f^\circ + \Delta v_f RT \ln\frac{p}{p^\circ}$	$\Delta G_f = \Delta G_f^\circ + \int_0^p \Delta v_f\, dp$	$\Delta G_{f,\,lq} = \Delta G_{f,\,s} = \Delta G_f$ (phase equilibrium)	

is found from the conditions

$$\frac{\partial F}{\partial a}=\frac{\partial F}{\partial b}=\frac{\partial F}{\partial c}=\frac{\partial F}{\partial d}=0$$

It is convenient to use the following notation (see [8]): $1 = x_0$, $T = x_1$, $T^2 = x_2$, $1/T^2 = x_3$, $C_p = y$, $(ij) = \sum_k x_{i,k}x_{j,k}$, $(iy) = \sum_k x_{i,k}y_k$. Therefore, the following holds:

$$\begin{aligned}
(00)\,a + (01)\,b + (02)\,c + (03)\,d &= (0y)\\
(10)\,a + (11)\,b + (12)\,c + (13)\,d &= (1y)\\
(20)\,a + (21)\,b + (22)\,c + (23)\,d &= (2y)\\
(30)\,a + (31)\,b + (32)\,c + (33)\,d &= (3y)
\end{aligned}$$

Let us designate the determinant of this system as

$$\begin{vmatrix} (00) & (01) & (02) & (03)\\ (10) & (11) & (12) & (13)\\ (20) & (21) & (22) & (23)\\ (30) & (31) & (32) & (33) \end{vmatrix} \equiv \Delta$$

and the determinants obtained from Δ by substituting the column (iy) for the column i as Δ_a, Δ_b, Δ_c, and Δ_d. Hence,

$$a=\frac{\Delta_a}{\Delta},\ b=\frac{\Delta_b}{\Delta},\ c=\frac{\Delta_c}{\Delta},\ d=\frac{\Delta_d}{\Delta}$$

For example, if the coefficients of the equation $C_p = a + bT$ are being determined, we have

$$\Delta=\begin{vmatrix} (00) & (01)\\ (10) & (11) \end{vmatrix},\quad \Delta_a=\begin{vmatrix} (0y) & (01)\\ (1y) & (11) \end{vmatrix},\quad \Delta_b=\begin{vmatrix} (00) & (0y)\\ (10) & (1y) \end{vmatrix}$$

and

$$a=\frac{\begin{vmatrix} (0y) & (01)\\ (1y) & (11) \end{vmatrix}}{\begin{vmatrix} (00) & (01)\\ (10) & (11) \end{vmatrix}}=\frac{\begin{vmatrix} \sum C_k^{ex} & \sum T_k\\ \sum C_{p,k}^{ex}T_k & \sum T_k^2 \end{vmatrix}}{\begin{vmatrix} n & \sum T_k\\ \sum T_k & \sum T_k^2 \end{vmatrix}}$$

$$b=\frac{\begin{vmatrix} (00) & (0y)\\ (10) & (1y) \end{vmatrix}}{\begin{vmatrix} (00) & (01)\\ (10) & (11) \end{vmatrix}}=\frac{\begin{vmatrix} n & \sum C_{p,k}^{ex}\\ \sum T_k & \sum T_kC_{p,k}^{ex} \end{vmatrix}}{\begin{vmatrix} n & \sum T_k\\ \sum T_k & \sum T_k^2 \end{vmatrix}}$$

It should be noted that modern computers include programmes for calculations by the method of least squares.

Let us see how numerical calculations are performed. The following results were obtained when measuring the heat capacity of a substance at standard pressure and various temperatures:

T, K	300	500	700	900
C_p°, J/(mol·K):				
experiment	24.40	26.88	29.35	31.83
calculated	24.34	26.81	29.29	31.76

It is necessary to obtain the coefficients a and b of the equation $C_p^\circ = a + bT$ and test its adequacy.

We use the method of least squares. We have: $(00) = 4$, $(01) = \sum T_k = 2.4 \times 10^3$, $(11) = \sum T_k^2 = 1.64 \times 10^6$, $(0y) = \sum C_{p,k}^{ex} = 112.46$, and $(1y) = \sum T_k C_{p,k}^{ex} = 699.52 \times 10^2$. Hence

$$\Delta = \begin{vmatrix} 4 & 2.4 \times 10^3 \\ 2.4 \times 10^3 & 1.64 \times 10^6 \end{vmatrix} = 6.56 \times 10^6 - 5.76 \times 10^6 = 0.8 \times 10^6$$

$$\Delta_a = \begin{vmatrix} 112.46 & 2.4 \times 10^3 \\ 699.52 \times 10^2 & 1.64 \times 10^6 \end{vmatrix} = 184.4 \times 10^6 - 167.9 \times 10^6 = 16.5 \times 10^6$$

$$\Delta_b = \begin{vmatrix} 4 & 112.46 \\ 2.4 \times 10^3 & 699.52 \times 10^2 \end{vmatrix} = 27.98 \times 10^4 - 26.99 \times 10^4 = 0.99 \times 10^4$$

$$a = \Delta_a/\Delta = 20.63, \quad b = \Delta_b/\Delta = 12.37 \times 10^{-3}$$

The calculated values of C_p° found by the equation $C_p^\circ = 20.63 + 12.37 \times 10^{-3}\, T$ are given in the third line of the above table under the experimental ones. The discrepancies between the calculated and experimental values are less than 0.3% and also less than the accuracy of the experiment. Consequently, there is no need of increasing the number of terms in the relation $C_p^\circ = C_p^\circ(T)$.

Naturally, if the discrepancies between the calculated and experimental values were substantial (their statistical estimation is treated, for example, in [8]), it would be necessary to investigate the equation $C_p^\circ = a + bT + cT^2$, and so on. To determine three coefficients, it is necessary to calculate third-order determinants, and the amount of calculations grows considerably. In this and more complicated cases, it is desirable to use computers.

Calculation of the Change in the Heat Capacity When the Pressure Changes. The following relation holds for any phase state (see p. 37):

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

For most solids and liquids, the temperature dependence of the

volume is described by the linear expression

$$v \approx \alpha + \beta T$$

Therefore, $(\partial^2 v/\partial T^2)_p \approx 0$, and the effect of the pressure on the heat capacity (at not very high pressures) is small, namely, $C_p^p \approx C_p^\circ$.

If the condensed state of a substance remains constant within a broad range of temperatures, a second-degree polynomial can be used for the temperature dependence of the volume:

$$v = \alpha + \beta T + \gamma T^2$$

In this case $(\partial C_p/\partial p)_T = \gamma T$ and at a constant temperature, the pressure dependence of C_p is linear:

$$C_p^p = C_p^\circ - \gamma T (p - p^\circ)$$

Since the values of γ are generally low, the influence of the pressure will be weak.

For example, the following expression was found for the molar volume of a solid (in m^3/kmol):

$$v = 0.345 - 1.76 \times 10^{-3} T + 0.29 \times 10^{-5} T^2$$

At 300 K, we have $(\partial C_p/\partial p)_T = -0.87 \times 10^{-3}$, i.e. an increase in the pressure by 1 MPa lowers the heat capacity by 870 J/(kmol·K), which is about 0.8% of the value of $C_p = 110 \times 10^3$ J/(kmol·K).

At very high pressures ($\Delta p \approx 100$ MPa), the heat capacity may change two and more times.

For an ideal gas, it follows from the equation of state (for one mole $v = RT/p$) that $(\partial^2 v/\partial T^2)_p = 0$, and the pressure does not affect the heat capacity.

For one mole of a real gas, we can use the equation $v = ZRT/p$. Finding $(\partial^2 v/\partial T^2)_p$ from it and going over to reduced parameters, we obtain

$$\left(\frac{\partial C_p}{\partial \pi}\right)_\tau = -\frac{R\tau}{\pi}\left[2\left(\frac{\partial z}{\partial \pi}\right)_\tau + \tau\left(\frac{\partial^2 Z}{\partial \pi^2}\right)_\tau\right] = \psi(\tau, \pi)$$

or

$$C_p^\pi - C_p^\circ = \int_{\pi^\circ}^{\pi} -\frac{R\tau}{\pi}\left[2\left(\frac{\partial Z}{\partial \pi}\right)_\tau + \tau\left(\frac{\partial^2 Z}{\partial \pi^2}\right)_\tau\right] d\pi = F(\tau, \pi) \quad (1.66)$$

The integral on the right-hand side of Eq. (1.66) can be taken graphically using the relation $Z = Z(\tau, \pi)$ given above (see Fig. 1).

Figure 7 presents $C_p^\pi - C_p^\circ$ as a function of π and τ for real gases plotted by graphical integration. By using this figure, it is easy to calculate the heat capacity of a real gas for elevated pressures.

Let us determine, for example, the change in the heat capacity of CO_2 if at 100 °C the pressure grows from 0.1 to 30 MPa. For carbon dioxide, $T_{cr} = 304$ K and $p_{cr} = 7.3$ MPa.

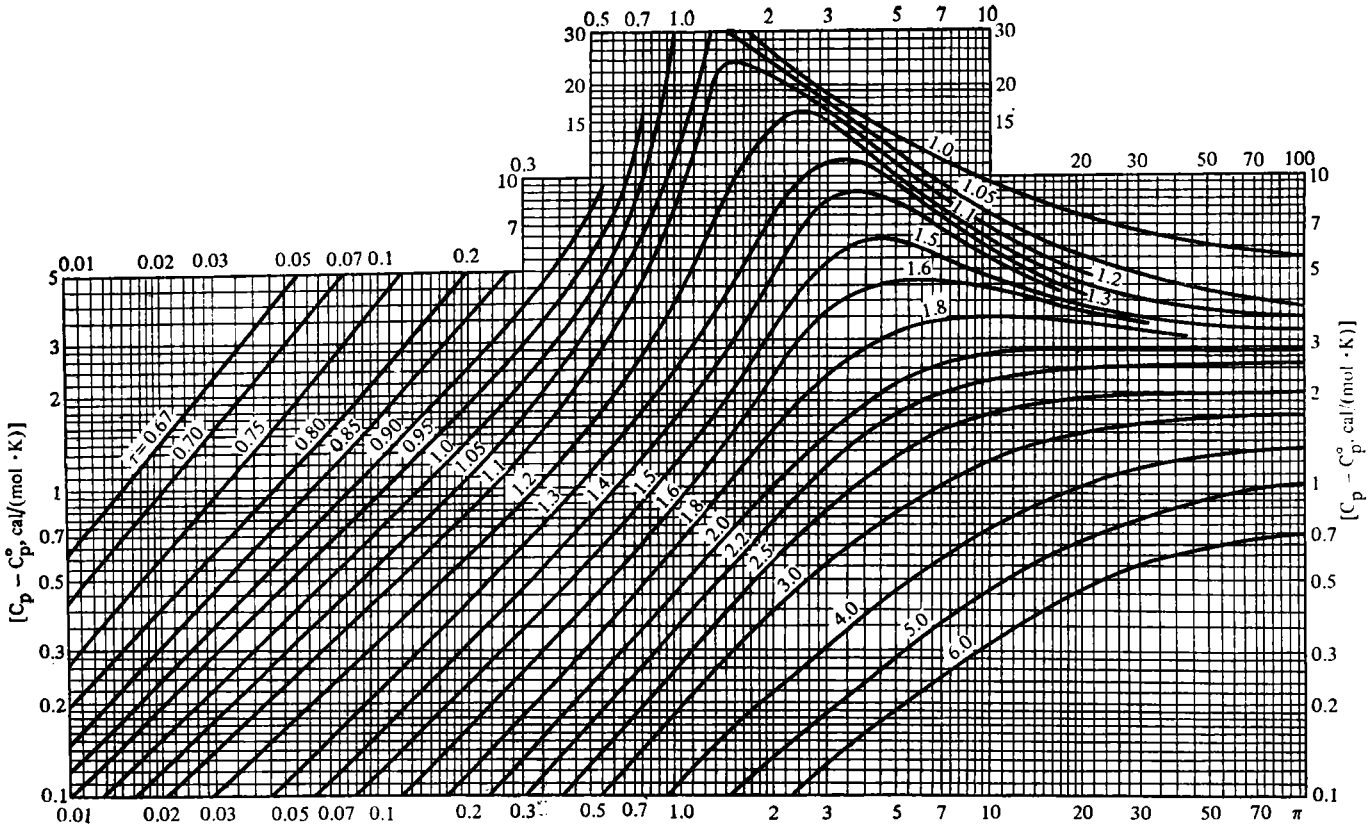
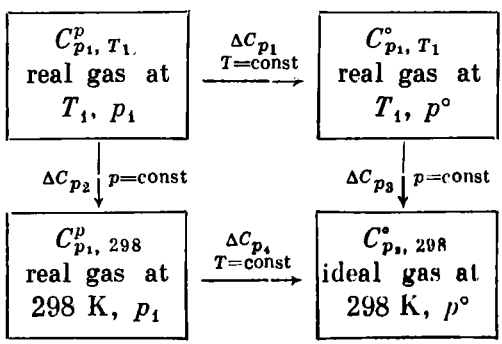


Fig. 7. Change in the heat capacity $C_p^{\pi} - C_p^0$ versus the reduced parameters τ and π (the numbers on the curves are the values of τ (1 cal = 4.184 J)

Consequently, $\tau = 373/304 = 1.23$, and π varies from 0.014 (practically from zero) to 4.11. We find from Fig. 7 that at $\tau = 1.23$ and $\pi = 4.11$, $C_p^{4.1} - C_p^\circ$ equals approximately 50 J/(mol·K).

It is interesting to note that generally at $\pi > 4$ the difference $C_p^\pi - C_p^\circ$ remains unchanged, namely, $C_p^{\pi > 4} - C_p^\circ \approx C_p^4 - C_p^\circ$. Moreover, which is important for our following treatment, $C_p^\pi - C_p^\circ$ practically equals zero at $\pi \leqslant 0.05$ and $\tau \geqslant 1.5$.

It is clear from the above how one can find the heat capacity of an ideal gas $C_{p_2}^\circ$ from that of a real gas $C_{p_1}^\circ$ and vice versa. Since the properties of a real and ideal gases coincide at low values of π ($\pi \leqslant 0.05$) and high values of τ ($\tau \geqslant 1.5$), i.e. when $Z \approx 1$ (see Figs. 2-6), we can use the following cycle:



$$C_{p_2,298}^\circ = C_{p_1,T_1}^p + \Delta C_{p_1} + \Delta C_{p_2} = C_{p_1,T_1}^p + \Delta C_{p_3} + \Delta C_{p_4}$$

Assume that we know the temperature dependence of the heat capacity of a real gas at the pressure p, namely, $C_{p_1}^p = a + bT + cT^2$ (the coefficient a does not have to be found).

Let us calculate the heat capacity at the temperature T_1 so that $\tau_1 = T_1/T_{cr}$ is at least 1.5 and use Fig. 7 to find the difference $\Delta C_p = C_p^\pi - C_p^\circ$. The heat capacity of an ideal gas at T_1 is $C_{p_2,T_1}^\circ = C_{p_1}^\pi - \Delta C_p$. Next we find $C_{p_2}^\circ$ for the arbitrary temperature T, using the same temperature dependence for the ideal gas as we did for the real gas.

Assume, for example, that for CO_2 (a real gas), we have established the relation

$$C_p(CO_2) = a + 9.04 \times 10^{-3}T - 8.54 \times 10^5 T^{-2}$$

and, further, that at 298 K and 30 MPa we have $C_p = 69.7$ J/(mol·K). The value of $\tau = 0.98$ corresponds to the temperature 298 K. Let us perform calculations for the temperature 456 K at which $\tau = 456/304 = 1.5$. Having determined a for a real gas at a pressure of 30 MPa from the above equation

$$[a = 69.7 - 9.04 \times 10^{-3} \times 298 + 8.54 \times 10^5 \times (298)^{-2} = 78.0],$$

we calculate the heat capacity of the real gas at 30 MPa and 456 K, i.e. at $\pi = 4.11$ and $\tau = 1.5$:

$$C_{456}^{4.11} = 78.0 + 9.04 \times 10^{-3} \times 456 - 8.54 \times 10^{5} \times 456^{-2} = 72.5 \text{ J/(mol·K)}$$

Now we find the change in the heat capacity when the reduced pressure grows from 0 to 4.11 at $\tau = 1.5$ from Fig. 7: $\Delta C_p = 6.78$ kcal (mol·K) ≈ 28.4 J/(mol × × K).

Consequently, the heat capacity of an ideal gas at $\tau = 1.5$ is

$$C_{p_2}^{\circ} = 72.5 - 28.4 = 44.1 \text{ J/(mol·K)}$$

Having found the coefficient a for an ideal gas ($a = 44.1 - 9.04 \times 10^{-3} \times \times 456 + 8.54 \times 10^{5} \times 456^{-2} = 44.1$), we determine the heat capacity of an ideal gas at 298 K:

$$C_{p_2}^{\circ} = 44.1 + 9.04 \times 10^{-3} \times 298 - 8.54 \times 10^{5} \times 298^{-2} = 37.2 \text{ J/(mol·K)}$$

This quantity can be used as a standard one for the ideal gas state of carbon dioxide at 298 K. If we want to go over from it to the heat capacity of a real gas, we perform the reverse procedures, namely, find ΔC_p for a growth in the pressure from Fig. 7 and calculate the change in the heat capacity with the temperature by the equation $C_p = C_p(T)$.

Thermodynamic tables give the heat capacities of substances in a hypothetic gaseous state for 298 K and standard pressure, although under these conditions a substance can exist in the form of a liquid or solid. Here the question arises as to how the value of $C_{p,298}^{\circ}$ given in the tables has been determined. For example, under the indicated conditions, benzene is a liquid and naphthalene is a solid, but their thermodynamic functions are given for the state of an ideal gas (see Appendix 2).

The answer is quite simple: since reactions are most frequently calculated for a high temperature in the gas phase, it is convenient to perform these calculations using the thermodynamic functions of gaseous substances instead of introducing relations taking account of the phase transitions. The heat capacity of gaseous benzene or any other condensed substance at 298 K is found by extrapolation of the experimental data obtained for higher temperatures when the substance is in the gas phase.

If, for example, for gaseous benzene we have found the equation

$$C_p^{\circ} = -33.91 + 472.19 \times 10^{-3}T - 298.56 \times 10^{-6}T^3 + 70.88 \times 10^{-9}T^3 \text{ J/(mol·K)}$$

from measurements within the interval 360-1400 K, it may also be employed for the temperature 298 K. At the same time, the equation of the heat capacity of liquid benzene holds only within a narrow temperature interval (281-353 K), and, as is noted in Table 3, is not related to the equation of C_p° for gaseous benzene.

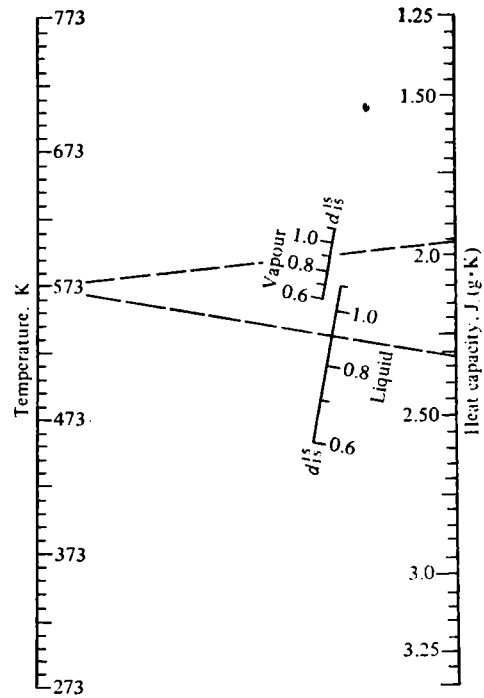


Fig. 8. Nomogram for determining the heat capacity of petroleum products (vapours and liquids)

The heat capacity of benzene vapour at 298 K can be found experimentally, but at a low pressure (the saturated vapour pressure of benzene at 298 K is 13 300 Pa). The conversion of this value to the standard pressure performed using the data of Fig. 7 results in virtually the same value as the extrapolation of the equation of $C_p^\circ(T)$ for a gas.

In the calculations of petroleum refining processes, the heat capacities of hydrocarbon mixtures are used. The treatment of experimental data has shown that at standard pressure, the heat capacity of a hydrocarbon mixture is determined by its temperature T and density relative to water at 15 °C, d_{15}, i.e. $C_p^\circ = C_p\,(T, d_{15}^{15})$. A nomogram for determining C_p° for liquid and gaseous hydrocarbon mixtures is presented in Fig. 8. If it is necessary to evaluate the heat capacity of a mixture for the pressure p noticeably differing from the standard pressure, one can use the procedure described for individual substances (see Fig. 7) by choosing T_{cr} and p_{cr} for the mixture according to the individual substance representing it. One can also use the relations given in Table 3, although this is less convenient.

Empirical relations are also available for the approximate calculation of the heat capacity of solids. Thus, for inorganic solids (sand, stone, cement, etc.), the following relation can be used:

$$C_p = 762.2 + 0.45\,(T - 273)\ \mathrm{J/(kg \cdot K)}$$

For coke, anthracite and bituminous coals, the recommended equation is

$$C_p = 838 + 3.69\,(T - 273) + 628.5\,x\ \mathrm{J/(kg \cdot K)}$$

where x is the fraction of volatile matter.

1.5. Calculations of the Entropy

Planck's postulate (the third law of thermodynamics) establishing that at 0 K the entropy of an ideal crystalline body equals zero allows us to determine the absolute value of the entropy of a substance at any temperature and pressure on the basis of thermochemical measurements and an equation of state.

Indeed, going over from the state of a substance at 0 K and p° to its state at an arbitrary temperature and pressure, we can write the following equations:

A. For a solid:

$$S^p_{T,\mathrm{s}} = \int_0^{T_1} \frac{C^\circ_{1,\mathrm{s}}}{T}\,dT + \frac{\Delta H^\circ_1}{T_1} + \int_{T_1}^{T_2} \frac{C^\circ_{2,\mathrm{s}}}{T}\,dT + \frac{\Delta H^\circ_2}{T_2} + \int_{T_2}^{T} \frac{C^\circ_{\mathrm{s}}}{T}\,dT - \int_{p^\circ}^{p} \left(\frac{\partial v_{\mathrm{s}}}{\partial T}\right)_p dp \qquad (1.67)$$

where T_1, T_2, ΔH°_1, and ΔH°_2 are the temperatures and heats of the allotropic transitions of the solid, respectively.

If such transitions do not occur, then $C^\circ_{1,\mathrm{s}} = C^\circ_{2,\mathrm{s}} = \ldots = C^\circ_{\mathrm{s}}$, and $\Delta H^\circ_1 = \Delta H^\circ_2 = \ldots = 0$. Near absolute zero, $C_{\mathrm{s}} = \mathrm{const} \times T^3$, hence $S_{\mathrm{s}} = \frac{1}{3}\,\mathrm{const} \times T^3$. The integrals can easily be found graphically from the experimental curves $C^\circ_{\mathrm{s}} = C^\circ_{\mathrm{s}}(T)$ and $v_{\mathrm{s}} = v_{\mathrm{s}}(T)$.

B. For a liquid:

$$S^p_{T,\,\mathrm{lq}} = S^\circ_{T_{\mathrm{m}},\mathrm{s}} + \frac{\Delta H^\circ_{\mathrm{m}}}{T_{\mathrm{m}}} + \int_{T_{\mathrm{m}}}^{T} \frac{C^\circ_{\mathrm{lq}}}{T}\,dT - \int_{p^\circ}^{p} \left(\frac{\partial v_{\mathrm{lq}}}{\partial T}\right)_p dp \qquad (1.68)$$

where $S^\circ_{T_{\mathrm{m}},\mathrm{s}}$ is the entropy of the solid at the melting point and standard pressure; it is calculated by Eq. (1.67). The integrals can be found graphically from the experimental curves $C^\circ_{\mathrm{lq}} = C^\circ_{\mathrm{lq}}(T)$ and $v_{\mathrm{lq}} = v_{\mathrm{lq}}(T)$.

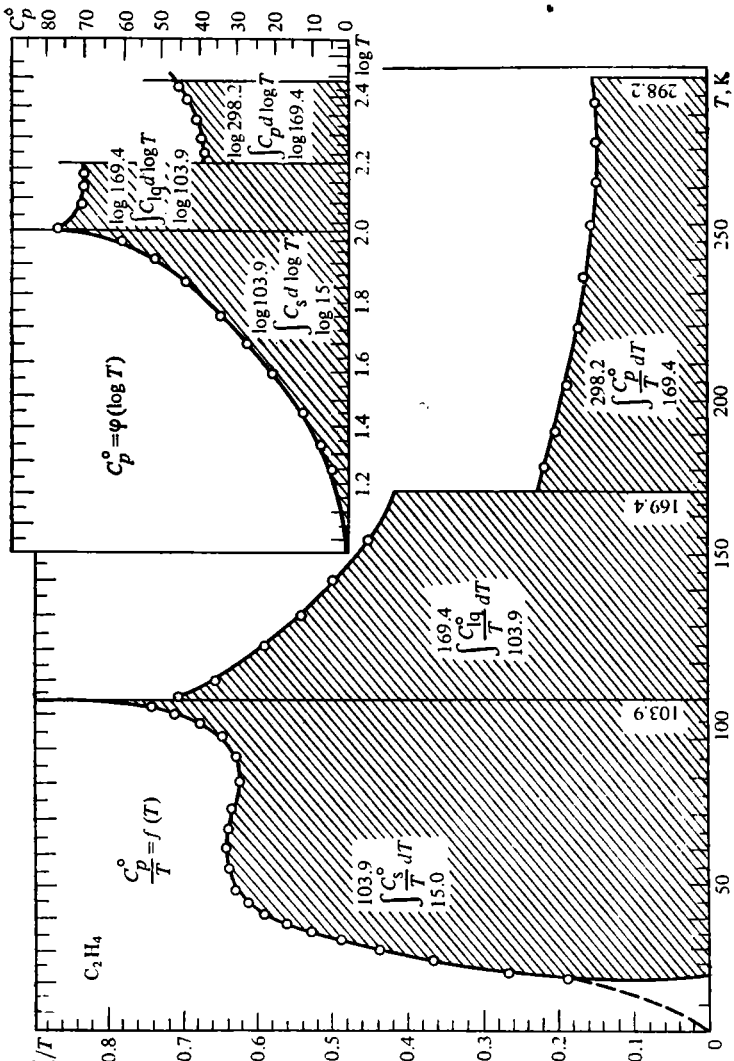


Fig. 9. Experimental relations $C_p^\circ/T = f(T)$ and $C_p^\circ = \varphi(\log T)$ for solid (s), liquid (lq), and gaseous ethylene used to calculate the entropy (the values of C_p° are in J/(mol·K))

C. For a real gas

$$S_T^p + S^\circ_{T_b,\mathrm{lq}} + \frac{\Delta H_b^\circ}{T_b} + \int_{T_b}^{T} \frac{C_p^\circ}{p} dT - \int_{p^\circ}^{p} \left(\frac{\partial v}{\partial T}\right)_p dp \qquad (1.69)$$

where $S^\circ_{T_b,\mathrm{lq}}$ is the entropy of the liquid at the boiling point (at standard pressure); it is calculated by Eq. (1.68). The integrals, as previously, can be found graphically.

For example, Fig. 9 presents experimental curves of C_p°/T as a function of T and C_p° as a function of $\log T$ for solid, liquid, and gaseous ethylene [9]. The hatched areas in the figure give the values of the integrals.

Thermodynamic tables give the values of the entropy for the hypothetic state of a substance in the form of an ideal gas. Let us see how the correction is determined when going over from the entropy of a real gas S^π to that of an ideal gas S^*. Since the properties of a real and ideal gases coincide at $p \to 0$, this correction is

$$\Delta S^* = -\int_0^p \left(\frac{\partial v}{\partial T}\right)_p dp \qquad (1.70)$$

For one mole of a real gas, we have $v = ZRT/p$. Using reduced parameters, we obtain

$$\Delta S^* = S^\pi - S^* = -R \int_0^\pi \left[\frac{Z}{\pi} + \frac{\tau}{\pi}\left(\frac{\partial Z}{\partial \tau}\right)_\pi\right] d\pi = \varphi(\tau, \pi) \qquad (1.71)$$

The integral can be found graphically from experimental curves of the compression factor Z as a function of the reduced parameters τ and π. The relevant calculations have been performed, and Fig. 10 gives the values of $S^* - S^\pi$ as a function of τ and π. For example, for ethylene ($T_{cr} = 283$ K, $p_{cr} = 5.05$ MPa) at 298 K and 0.1 MPa, we have $\tau = 1.09$ and $\pi = 0.2$. From Fig. 10, we find $S^* - S^\pi \approx 0.8$ J/(mol·K).

Thus, using the data for ethylene, we obtain for $S_{15,8} = 1.0$ J/(mol·K) the following values of ΔS [in J/(mol·K)]:

Heating of solid ethylene to melting point (103.9 K) (see Fig. 9) . . .	51.1
Heating of liquid ethylene to boiling point (169.4 K) (see Fig. 9)	33.2
Melting ($\Delta H_m^\circ = 3350$)	32.2
Vaporization ($\Delta H_v^\circ = 13\,543.6$)	79.9
Heating of gaseous ethylene to 298 K (see Fig. 9)	21.5
Correction for transition to an ideal gas	~0.8
Entropy of ethylene at 298 K in the state of an ideal gas	219.7

The obtained value can be included in standard tables (see, for example, the value of S° for ethylene at 300 K in Table A.21, Ap-

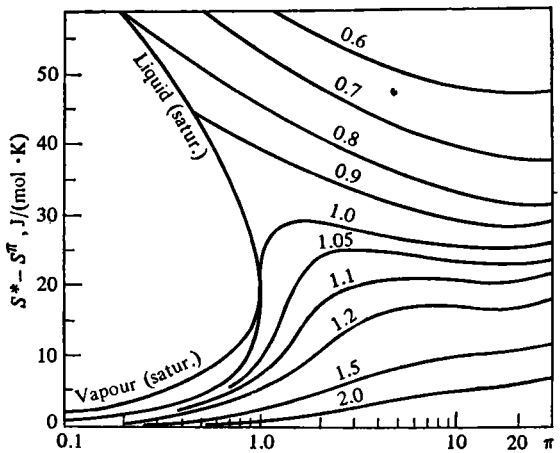
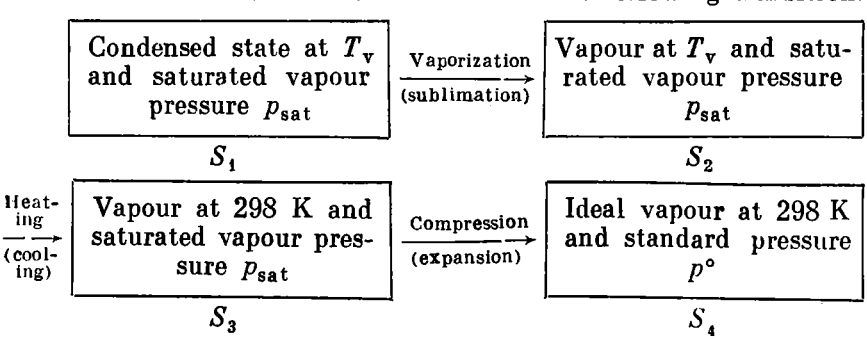


Fig. 10. Entropy of real substances as a function of the reduced pressure and temperature.

S^π and S^* are the entropies of a substance at the reduced pressure and in the state of an ideal gas at standard pressure ($S^* = S^\pi_{\pi \to 0}$); $z_{cr} = 0.27$. (The numbers on the curves are the values of τ)

pendix 2). If we are to find the entropy of a real gas from the tabulated value of the entropy for the state of an ideal gas, we must subtract $S^* - S^\pi$ from the latter according to Fig. 10 (i.e. 0.8 for ethylene). A transition to the liquid state lowers the value of the entropy for a gas by the change in the entropy caused by boiling and heating of the vapour.

We have already noted that thermodynamic tables give the functions for liquids or solids (benzene, naphthalene, etc.) at 298 K in the hypothetic state of an ideal gas. The entropy of this hypothetic state can be calculated on the basis of the following transition:



The value of S_1 is calculated by the relations given in paragraphs A and B. It is also not difficult to determine the other quantities be-

cause

$$S_2 - S_1 = \Delta H_v / T_v, \quad S_3 - S_2 = \int_{T_v}^{298} \frac{C_p}{T} dT$$

$$S_4^\circ - S_3 = -\int_{p_{sat}}^{p^\circ} \left(\frac{\partial v}{\partial T}\right) dp, \quad S_4^\circ = S_1 + (S_2 - S_1) + (S_3 - S_2) + (S_4^\circ - S_3)$$

Let us compare for one mole of carbon dioxide the change in the entropy in isothermal (100 °C) compression from 0.1 to 100 MPa, assuming first the state of an ideal gas, then that of a real gas, and using the compression factor (see Fig. 1).

A. For an ideal gas

$$S_2^* - S_1^* = \Delta S_p^* = -\int_{0.1}^{100} \left(\frac{\partial v}{\partial T}\right)_p dp = -\int_{0.1}^{100} R d \ln p = -R \ln 1000 = -57.40 \text{ J/(mol·K)}$$

B. For carbon dioxide, $T_{cr} = 304$ K and $p_{cr} = 7.3$ MPa. Hence, for the initial state, we have $\tau_1 = 373/304 = 1.23$, $\pi_1 = 0.1/7.3 = 0.014$, and for the final state $\tau_2 = 1.23$ and $\pi_2 = 13.70$.

In Fig. 10, we find $S_1 - S_1^* = 0$ for the initial state, and $S_2 - S_2^* = -15.90$ J/(mol·K) for the final state. Consequently,

$$S_2 - S_1 = (S_2 - S_2^*) - (S_1 - S_1^*) + (S_2^* - S_1^*) = -15.90 - 0 - 57.40 = -73.30 \text{ J/(mol·K)}$$

Hence, the taking into consideration of the properties of a real gas changes the value of ΔS_p by −15.9 J/(mol·K). If from standard thermodynamic tables we have found the entropy of CO_2 to be 222.2 J/(mol·K) for the state of an ideal gas at 0.1 MPa and 373 K, then at the same temperature and pressure in the state of a real gas the entropy will be practically the same ($S_1 - S_1^* = 0$), while at the same temperature and 100 MPa it will decrease by 73.3 J/(mol·K), i.e. will be 148.9 J/(mol·K).

The above example shows how the entropy is calculated for high pressures and how it is determined for a real state from tabulated data for the state of an ideal gas.

1.6. Calculations of the Enthalpy

The calculations of the change in the enthalpy for an isobaric change in the temperature are based on the relation

$$_T - H_{T_0} = \int_{T_0}^{T} C_p dT$$

It is not difficult to perform these calculations when the heat capacity of a substance is given in the explicit form, for example, $C_p = a + bT + cT^2$, and a number of examples of such calculations

are given in following chapters. The object of the present section is to calculate the enthalpies (the change in the enthalpies) ΔH_c and ΔH_f of a substance in the real state from the data on the standard enthalpies (changes in the enthalpies) in the state of an ideal gas (ΔH_c°, ΔH_f°) given in standard thermodynamic tables. It follows from the expression

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p + v$$

given on p. 37 that in the state of an ideal gas (for one mole $v = RT/p$), the quantity $(\partial H/\partial p)_T = 0$ and does not depend on the pressure. For a real gas,

$$v = \frac{ZRT}{p} \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_T = -\frac{RT^2}{p}\left(\frac{\partial Z}{\partial T}\right)_p$$

Going over to reduced parameters, we obtain

$$\frac{\Delta H_p}{T_{cr}} = -R\tau^2 \int_{\pi_1}^{\pi_2} \left(\frac{\partial Z}{d\tau}\right)_\pi d\ln\pi \qquad (1.72)$$

If the relation $Z = Z(\tau, \pi)$ has been obtained (see Fig. 1), we can also calculate the value of the integral in Eq. (1.72). It is convenient to perform integration by choosing $\pi_1 \to 0$, when a real gas behaves like an ideal one. This will give us the difference between the enthalpies of a real H and ideal H^* gases:

$$\frac{H^* - H}{T_{cr}} = -\frac{H - H^*}{T_{cr}} = R\tau^2 \int_0^{\pi} \left(\frac{\partial Z}{\partial \tau}\right)_\pi d\ln\pi$$

If $Z = Z(\tau, \pi, Z_{cr})$, the quantities $(H^* - H)/T_{cr}$ also depend on τ, π, and Z_{cr}, namely, $(H^* - H)/T_{cr} = \varphi(\tau, \pi, Z_{cr})$. This relation is given in Fig. 11 for the most widespread class of substances ($Z_{cr} = 0.27$). Table 4 gives the values of $(H^* - H)/T_{cr}$ for the typical values of Z_{cr} listed on a previous page, namely, 0.23, 0.25, 0.27, and 0.29. The data of this table enable one to perform sufficiently accurate calculations of the heats of the reactions of any substances at high pressures.

The heats of formation (or combustion) of substances at a high pressure can be calculated from standard tabulated data and the relations $(H^* - H)/T_{cr} = \varphi(\tau, \pi, Z_{cr})$.

Assume, for example, that the heat of formation of methane from graphite and hydrogen at standard pressure and 400 K is given in a standard thermodynamic table, namely, $\Delta H_f^\circ = -77.95$ kJ/mol (see Table A.21, Appendix 2), and it is necessary to determine the heat of formation of methane at the same temperature, but at 100 MPa, i.e. ΔH_f^{100}. We shall use the following isothermal cycle

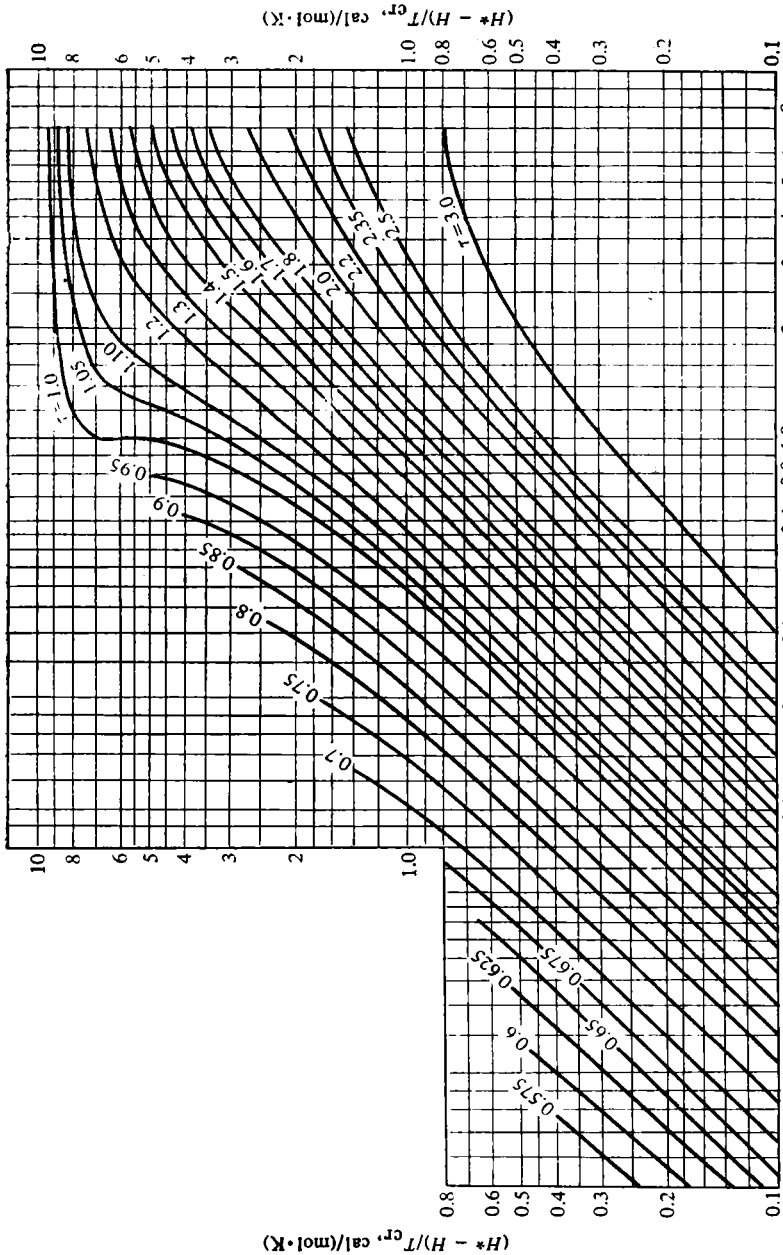


Fig. 11. Enthalpy of real substances as a function of the reduced pressure and temperature (1 cal = 4.184 J). H and H^* are the enthalpies of a substance at the reduced pressure π and in the state of an ideal gas, respectively

Table 4. **Values of $(H^* - H)/T_{cr}$ for Gases and Liquids in J/(mol·K) [3] (the numbers to the left of the dotted line are values for the liquid state)**

π	$Z_{cr} = 0.23$ at $\tau =$					
	0.5	0.7	0.9	1.1	1.5	1.7
0.1	66.26	57.81	1.52	0.81	0.38	—
0.3	66.16	57.76	5.65	2.57	1.11	0.86
0.5	66.06	57.68	47.18	4.53	1.88	1.42
0.7	65.96	57.62	47.40	6.77	2.68	2.01
0.9	65.88	57.56	47.53	9.31	3.47	2.58
1.1	65.77	57.48	47.69	12.33	4.20	3.23
1.3	65.64	57.41	47.79	15.92	5.11	3.64
1.5	65.53	57.35	47.87	20.01	6.03	5.71

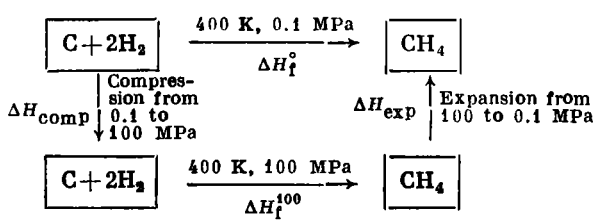
	$Z_{cr} = 0.25$					
	0.5	0.7	0.9	1.1	1.5	2.0
0.1	65.93	56.93	1.51	0.74	0.38	0.13
0.3	65.93	56.93	5.90	2.30	0.92	0.42
0.5	65.80	57.01	43.99	4.27	1.72	0.71
0.7	65.72	56.97	44.25	6.49	2.60	1.17
0.9	65.64	57.10	44.54	9.08	3.43	1.63
1.2	65.51	56.51	44.83	13.56	5.06	2.22

	$Z_{cr} = 0.27$						
	0.5	0.7	0.9	1.1	1.5	2.0	3.0
0.1	62.0	52.41	1.26	0.96	0.33	0.12	0.12
0.5	62.04	52.53	41.44	5.52	1.59	0.71	0.54
1.0	62.0	52.58	41.64	24.28	3.81	1.80	0.79
1.5	61.95	52.41	42.53	34.49	6.11	2.76	1.09
2.0	61.95	52.28	43.07	36.38	8.08	3.68	1.34
3.0	61.78	51.61	43.12	37.30	12.22	5.65	1.80
5.0	—	—	42.78	38.22	16.32	8.58	2.55
10.0	—	—	41.15	37.76	18.75	10.98	2.64
20.0	—	—	36.59	33.74	15.82	8.24	—1.05
30.0	—	—	31.73	29.05	11.72	3.93	—7.45

Table 4 (*concluded*)

	4.0	6.0	10.0	15.0		
2.0	0.46	0.08	0.00	0.12		
3.0	0.84	0.17	0.00	0.29		
5.0	1.42	0.42	0.00	0.46		
10.0	0.59	0.17	0.00	0.71		
20.0	−0.96	−0.59	0.00	0.59		
30.0	−6.20	−2.01	−0.54	0.29		
	$Z_{cr} = 0.29$					
	0.5	0.7	0.9	1.1	1.5	2.0
0.1	46.88	42.15	1.05	0.54	0.29	0.12
0.3	46.88	42.46	3.14	1.55	0.80	0.42
0.5	46.67	42.36	6.87	3.55	1.51	0.71
0.7	46.42	42.61	37.55	5.23	2.34	1.17
0.9	46.05	42.91	37.26	7.33	3.10	1.63
1.2	45.75	43.74	38.09	11.39	4.65	2.13

for our calculations:



Since $\Delta H_f^{100} = \Delta H_f^\circ - (\Delta H_{comp} + \Delta H_{exp})$, we have to find the heats of compression of two moles of hydrogen from 0.1 to 100 MPa and the heat of expansion of one mole of methane from 100 to 0.1 MPa.

For hydrogen, $T_{cr} = 33.3$ K, $p_{cr} = 1.3$ MPa, and $Z_{cr} = 0.29$, hence, $\tau_2 = \tau_1 = T/(T_{cr} + 8) = 400/41 \approx 9.8$, $\pi_1 = p_1/(p_{cr} + 0.8) = 0.1/2.1 \approx 0.05$, and $\pi_2 = 100/2.1 = 47.6$

For methane, $T_{cr} = 191$ K, $p_{cr} = 4.6$ MPa, and $Z_{cr} = 0.29$, hence, $\tau_2 = \tau_1 = T/T_{cr} = 400/191 = 2.1$, $\pi_1 = p_1/p_{cr} = 100/4.6 = 21.7$, and $\pi_2 = 0.1/4.6 = 0.02$.

From reference data on the value of $(H^* - H)/T_{cr}$ as a function of π, τ, and Z_{cr}, for 400 K and 0.1 MPa we have

$$H_1^*(H_2) - H_1(H_2) \approx H_2^*(CH_4) - H_2(CH_4) = 0$$

for 400 K and 100 MPa,

$$H_2^*(H_2) - H_2(H_2) = -2.1 \times 33 = -70 \text{ J/mol}$$

$$H_1^*(CH_4) - H_1(CH_4) = 10.5 \times 191 = 2000 \text{ J/mol}$$

Having in view that $H_1^*(H_2) = H_2^*(H_2)$ and $H_1^*(CH_4) = H_2^*(CH_4)$, we obtain

$$\Delta H_{comp} = 2\,[H_2(H_2) - H_1(H_2)] = 2\,(0 - 0.07) = -0.14 \text{ kJ/mol}$$

$$\Delta H_{exp} = H_2(CH_4) - H_1(CH_4) = 2 \text{ kJ/mol}$$

Consequently, $\Delta H_f^{100} = -77.95 - 0.14 + 2 = -76.09$ kJ/mol

Calculations show that the effect of the pressure on the heat of formation of compounds is negligible. This is associated with the fact that in most cases the quantities ΔH_{comp} and ΔH_{exp} are opposite in sign and eliminate each other. Only in rare cases at pressures up to 100 MPa do the differences in the heats of formation at the standard and increased pressures exceed 15 kJ/mol, while in most cases it is less than 10 kJ/mol, i.e. 3%. We shall illustrate this with additional data for carbon dioxide. At 100 °C and standard pressure, its heat of formation is —394 kJ/mol. The heats of expansion of oxygen at this temperature from 100 MPa to 0.1 MPa and of compression of CO_2 from 0.1 to 100 MPa are 0.6 and —8.1 kJ/mol, respectively. When the pressure grows 1000 times, the heat of formation of CO_2 changes by —7.5 kJ/mol, i.e. by 2%.

Processes under pressure are often conducted in closed systems. When calculating them, we have to evaluate ΔU from data on the values of ΔH. These calculations involve no difficulties because for real systems we have

$$\Delta U = \Delta H - \Delta(pv) = \Delta H - RT\Delta Z$$

Assume, for example, that we have determined the change in the enthalpy in the compression of carbon dioxide from 0.1 to 100 MPa at 100 °C. It is —8.1 kJ/mol. The change in the internal energy corresponding to this process is

$$\Delta U = -8.1 - 8.31 \times 10^{-3} \times 373\,(1.42 - 1) = -9.4 \text{ kJ/mol}$$

1.7. Calculations of the Gibbs and Helmholtz Energies and of the Equilibrium Constant

The changes in the functions A (the Helmholtz energy) and G (the Gibbs energy) are calculated from the relevant changes in the functions U, H, and S. As applied to reactions, the changes in the functions are called the functions of a reaction, namely, the Gibbs energy of a reaction, the enthalpy of a reaction, etc.

The following relations hold:

$$\Delta A = \Delta U - T\Delta S,\ \Delta G = \Delta H - T\Delta S$$

The quantities ΔA and ΔG are used to determine both the thermodynamic probability of a process (a process occurs from the left to the right at T, v = const if $\Delta A < 0$, or at T, p = const if $\Delta G < 0$)

and the equilibrium constant (from the equation of an isotherm), and further the equilibrium composition. The data given in thermodynamic tables can be used to calculate the standard enthalpy ΔH° and entropy ΔS° of a reaction.

If the properties of the components differ substantially from ideal ones, the quantities ΔH° and ΔS° are converted to the real state as shown above, and ΔH and ΔS are found.

It is simple to find the value of ΔA from ΔG because $\Delta A = \Delta G - p\Delta v$. For reactions in the condensed phase, $p\Delta v \approx 0$, whereas in an ideal gaseous phase $p\Delta v$ depends on the change in the number of moles:

$$p\,\Delta v = \left(\sum \nu_i\right) RT$$

In a real gas phase, $p\Delta v$ depends additionally on the compression factors:

$$p\,\Delta v = \left(\sum \nu_i Z_i\right) RT$$

When using the data of standard thermodynamic tables containing the characteristics of substances in the state of an ideal gas, it is the simplest to determine the standard Gibbs energy of a reaction:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

To simplify calculations, many tables give the values of the standard Gibbs energies of formation of compounds:

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$$

or the logarithms of the standard equilibrium constants of formation of compounds:

$$\log K_{p,f}^\circ = -\frac{\Delta G_f^\circ}{2.303RT} \tag{1.73}$$

It is easy to find ΔG° or K_p° for a reaction from the values of ΔG_f^0 or $\log K_{p,f}^\circ$ for the components of the reaction mixture:

$$\Delta G^\circ = \sum \nu_i\, \Delta G_{f,i}^\circ, \qquad \log K_p^\circ = \sum \nu_i \log K_{p,f,i}^\circ$$

It is convenient to use the equilibrium constant K_x (see below) for calculating the equilibrium composition. The transition to this constant from the constant K_p° calculated by the data of thermodynamic rables is performed for gas systems using the following expression:

$$K_x = \frac{K_p}{K\gamma p^{\sum \nu_i}} = \frac{K_p^\circ}{K\gamma}\left(\frac{p^\circ}{p}\right)^{\sum \nu_i} \tag{1.74}$$

Standard Change in Gibbs Energy, Standard Equilibrium Constant. Thermodynamic tables give the thermodynamic functions of substances measured at or calculated for the standard pressure $p^\circ =$

= 101 325 Pa (1 atm), namely, the heat capaciy C_p°, entropy S°, enthalpy (heat) of formation ΔH_f°, enthalpy (heat of combustion) ΔH_c°, Gibbs energy of formation ΔG_f°, and the logarithm of the equilibrium constant of formation $\log K_{p,f}^\circ$. These quantities are used to find the standard Gibbs energy ΔG° of the reaction being studied, and from it the equilibrium constant K_p° and the equilibrium composition:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_p^\circ$$

Let us now consider the units in which the equilibrium constant is measured.

It should be remembered that for a reaction the equilibrium constant K in the general case is a dimensional quantity. Indeed, if the reaction

$$-\nu_1 A_1 - \nu_2 A_2 - \ldots + \nu_1' A_1' + \nu_2' A_2' + \ldots = 0$$

is conducted in the gas phase, we have

$$K_p = \prod p_i^{\nu_i} \quad \text{and} \quad [K_p] = [p]^{\sum \nu_i} = (\text{Pa})^{\sum \nu_i}$$

where the brackets are the symbol of the dimension of a quantity, and $\sum \nu_i$ is the change in the number of moles in the reaction.

Only in a particular case when $\sum \nu_i = 0$ are the equilibrium constants K_f, K_c, and K_p dimensionless [see Eqs. (1.29) and (1.30)]. Naturally, only the constants K_x expressed in terms of the mole fractions are always dimensionless [see Eq. (1.31)].

Isotherm equation (1.38a) for the case when the initial mixture contains reactants with partial pressures equal to the standard pressure p° has the form

$$\Delta G^\circ = RT\left[\ln \prod (p^\circ)^{\nu_i} - \ln K_p\right] = -RT \ln \prod \left(\frac{p_i}{p^\circ}\right)^{\nu_i}$$
$$= -RT \ln \frac{K_p}{(p^\circ)^{\sum \nu_i}}$$

Here p_i is the equilibrium partial pressure of substance A_i.

It is recommended [10] to introduce the notation $\prod (p_i/p^\circ)^{\nu_i} = K_p^\circ$ and call K_p° the standard equilibrium constant. Hence,

$$\Delta G^\circ = -RT \ln K_p^\circ \tag{1.75}$$

where $K_p^\circ = K_p/(p^\circ)^{\sum \nu_i}$ [consequently, $K_p = K_p^\circ (p^\circ)^{\sum \nu_i}$]. Unlike K_p, the constant K_p° is always a dimensionless quantity. It is exactly Eq. (1.75) (and not the equation $\Delta G^\circ = -RT \ln K_p$ given in a number of publications) that is the strict one. If the pressure is measured in atmospheres, i.e. $p^\circ = 1$ atm, then $K_p = K_p^\circ$, and the equation $\Delta G^\circ = -RT \ln K_p$ enables one to find the numerically

correct value of K_p. If SI units are employed and the pressure is expressed in pascals, Eq. (1.75) must be used.

Thus, when K_p is being calculated from the value of ΔG°, we must take into account that the following expressions hold:

$$K_p = \begin{cases} \exp\left(-\frac{\Delta G^\circ}{RT}\right), & (\text{atm})^{\sum \nu_i} \\ \left[\exp\left(-\frac{\Delta G^\circ}{RT}\right)\right] (101\ 325)^{\sum \nu_i}, & (\text{Pa})^{\sum \nu_i} \end{cases}$$

For example, for the gas-phase reaction $-C_2H_2 - 2H_2 + C_2H_6 = 0$ ($\sum \nu_i = -1 - 2 + 1 = -2$):

$$K_p = \begin{cases} \exp\left(-\frac{\Delta G^\circ}{RT}\right), & (\text{atm})^{-2} \\ \left[\exp\left(-\frac{\Delta G^\circ}{RT}\right)\right] (101\ 325)^{-2}, & (\text{Pa})^{-2} \end{cases}$$

Relation Between Equilibrium Constant and Equilibrium Degree of Conversion. In the overwhelming majority of cases, thermodynamic calculations allow one to determine the constant K_x expressed in terms of the mole fractions x_{A_i} of the reactants in an equilibrium mixture for the reaction $\nu_i A_i = 0$.

$$K_x = \frac{x_{A_1'}^{\nu_1'} x_{A_2'}^{\nu_2'} \cdots}{x_{A_1}^{\nu_1} x_{A_2}^{\nu_2} \cdots} = \prod x_{A_i}^{\nu_i}$$

(the stoichiometric coefficients ν_i are positive for the products and negative for the reactants; $\sum \nu_i \equiv \Delta\nu$ is the change in the number of moles in a reaction). Next the task arises of finding the unknown quantities x_{A_i}.

It is clear that we cannot find several unknowns x_{A_i} from one equation, so now we have to invoke additional equations for the number of equations to equal the number of unknowns.

It will be most convenient to introduce a new variable—the degree of conversion of one of the reactants (A_l), namely, y. We shall determine the degree of conversion as the fraction of A_l that has reacted; this quantity is convenient for characterizing the possible extent of a reaction.

If $m_{0,i}$ is the number of moles of the component A_i in the initial mixture, m_i is the number of moles of the same component in the equilibrium mixture, while the ratio of the numbers of moles of the components A_i and A_1 in the initial mixture $m_{0,i}/m_{0,1} = \delta_i$, we have:

$$y = \frac{m_{0,1} - m_1}{m_{0,1}}, \quad m_i = m_{0,1}\left(\delta_i + \frac{\nu_i}{\nu_1} y\right), \quad \delta_1 \equiv 1$$

Hence,

$$x_{A_1} = \frac{m_{0,1}(1-y)}{\sum m_i},$$

$$x_{A_2} = \frac{m_{0,1}\left(\delta_2 + \frac{\nu_2}{\nu_1} y\right)}{\sum m_i}, \quad \ldots, \quad x_{A_1'} = \frac{m_{0,1}\left(\delta_1' + \frac{\nu_1'}{\nu_1} y\right)}{\sum m_i}, \ldots$$

$$\sum m_i = m_{0,1}\left(1 + \delta_2 + \ldots + \delta_1' + \delta_2' + \ldots + \frac{\sum \nu_i}{\nu_i} y\right)$$

$$= m_{0,1}\left(\sum \delta_i + \frac{\sum \nu_i}{\nu_1} y\right)$$

Consequently, we obtain the following equation for determining one unknown quantity y:

$$K_x = \frac{\left(\delta_1' + \frac{\nu_1'}{\nu_1} y\right)^{\nu_1'} \left(\delta_2' + \frac{\nu_2'}{\nu_1} y\right)^{\nu_2'} \ldots}{(1+y)^{\nu_1} \left(\delta_2 + \frac{\nu_2}{\nu_1} y\right)^{\nu_2} \left(\sum \delta_i + \frac{\sum \nu_i}{\nu_1} y\right)^{\sum \nu_i}} \tag{1.76}$$

In most cases, not over two reactants enter into a chemical reaction, and not over two products form, i.e. a reaction follows the equation:

$$-\nu_1 A_1 - \nu_2 A_2 + \nu_1' A_1' + \nu_2' A_2' = 0$$

For such a sufficiently general reaction, we have $\sum \nu_i = -\nu_1 - \nu_2 + \nu_1' + \nu_2'$, and the following equation holds:

$$K_x = \frac{\left(\delta_1' + \frac{\nu_1'}{\nu_1} y\right)^{\nu_1'} \left(\delta_2' + \frac{\nu_2'}{\nu_1} y\right)^{\nu_2'}}{(1-y)^{\nu_1} \left(\delta_2 - \frac{\nu_2}{\nu_1} y\right)^{\nu_2}} \frac{1}{\left(1 + \delta_2 + \delta_1' + \delta_2' + \frac{\sum \nu_i}{\nu_1} y\right)^{\sum \nu_i}} \tag{1.77}$$

Some particular cases of this equation are given in Table 5.

In all cases, the value of y is the larger, the larger is the constant K_x, i.e. it increases with the temperature for endothermic and decreases for exothermic reactions.

The influence of the pressure on the value of y is determined by its influence on K_x. Thus, for reactions in an ideal gas mixture, we have

$$K_x = K_p p^{-\sum \nu_i}$$

Table 5. **Equations for Calculating the Equilibrium Constant and Equilibrium Degree of Conversion***

Reaction	Equilibrium constant, K_x	Equilibrium degree of conversion y
$A_1 \rightarrow A_1' + A_2'$, $\sum \nu_i = 1$ (cracking, dehydrogenation, cyclization of alkanes to cycloalkanes, etc.)	$K_x = \frac{y^2}{1-y^2}$	$y = \sqrt{\frac{K_x}{1+K_x}}$
$A_1 \rightarrow A_1'$, $\sum \nu_i = 0$ (isomerization)	$K_x = \frac{y}{1-y}$	$y = \frac{K_x}{1+K_x}$
$A_1 \rightarrow A_1' + 3A_2'$, $\sum \nu_i = 3$ (dehydrogenation of six-membered cycloalkanes)	$K_x = \frac{27y^4}{(1-y)(1+3y)^3}$	Determined by numerical search
$A_1 + A_2 \rightarrow A_1' + A_2'$, $\sum \nu_i = 0$ (hydrocracking of alkanes, etc.)	$K_x = \frac{y^2}{(1-y)^2}$	$y = \frac{K_x - \sqrt{K_x}}{K_x - 1}$
$A_1 + A_2 \rightarrow A_1'$, $\sum \nu_i = -1$ (hydrocracking of cycloalkanes, alkylation)	$K_x = \frac{y(2-y)}{(1-y)^2}$	$y = \frac{K_x + 1 - \sqrt{2K_x}}{K_x + 1}$

* The initial mixture contains no products ($\delta_1' = \delta_2' = 0$), the ratio of the reactant moles is stoichiometric ($\delta_2 = \nu_2/\nu_1$).

If $\sum \nu_i = 0$, K_x and y do not depend on the pressure. When $\sum \nu_i > 0$, K_x and y decrease with a growth in the pressure, and when $\sum \nu_i < 0$, they increase.

But the equilibrium degree of conversion y of substance A_1, unlike K_x, also depends on the initial composition of the mixture, i.e. on the value of δ_i. The presence of products in the initial mixture lowers y, while its dilution with other reactants increases it. The influence of δ_i on y is of a major significance for the technical embodiment of chemical processes. Specific examples of calculating y for various values of δ_i are contained in following sections. It should only be noted here that although the equation $K_x = f(y)$ is non-linear relative to y and can have several solutions, only one value of y exists that has a physical meaning. This follows from the condition of the uniqueness of the state of equilibrium (see Chap. 3).

Chapter 2

Calculations of Heats, Equilibrium Constants, and Equilibrium Compositions of Simple Reactions

2.1. Errors of Thermodynamic Calculations

The thermodynamic functions (C_p°, ΔH_c° and others) that are the initial quantities for thermodynamic calculations and are measured in an experiment or estimated by approximate methods are found with errors that may grow in the thermodynamic calculations. It is therefore desirable to evaluate the possible error of the calculations. Thermodynamic calculations are generally performed using algebraic relations of the form $z = f(u_1, \ldots, u_k)$, where z is the quantity being calculated, while $u_1, \ldots, u_k$ are arguments for which the standard errors $s_{\bar{u}_i}$ or variances $s^2_{\bar{u}_i}$ are other than zero. Correct calculations presume the finding of both the value of z (in a statistical meaning—estimation of the value of z) and the standard error of the calculations s^2_z.

The values of $s_{\bar{u}_i}$ are found experimentally, performing n parallel measurements, by the expression

$$s^2_{\bar{u}_i} = \frac{\sum_j (\bar{u}_i - u_{ij})^2}{n(n-1)} \tag{2.1}$$

where $\bar{u}_i = \sum_j u_{ij}/n$.

The following expression holds for s^2_z [8]:

$$s^2_z = \sum_i \left(\frac{\partial f}{\partial u_i}\right)^2 s^2_{\bar{u}_i} \tag{2.2}$$

For simplification, below we shall use the symbols s_z and s_{u_i}. Let us define the confidence interval as the region of values containing the true value of the quantity being calculated and ranging from $z - \Delta z$ to $z + \Delta z$. For a given probability and the customarily ob-

served normal distribution law, we have [8]:

at a probability of 0.9, or 90% $\Delta z = 1.65\sqrt{s_z^2}$

at a probability of 0.95, or 95% $\Delta z = 1.96\sqrt{s_z^2}$

at a probability of 0.99, or 99% $\Delta z = 2.58\sqrt{s_z^2}$

We can understand the probability as the fraction of parallel measurements (replications) in which the quantity being measured does not leave the limits of the confidence interval. The above relations are observed if the number of parallel measurements is large [8]. But even with a small number of measurements, if they can be considered representative (there is no "shifting" of the results), the same relations are used for calculations.

In calculations in the field of chemical technolcgy, a probability of 0.95 is used most frequently. Here all deviations from the calculated quantity exceeding $1.96\sqrt{s_z^2}$ are considered to be improbable, and this value determines the limiting error of the calculations, namely, $\Delta_{\lim} z = 1.96\sqrt{s_z^2} \approx 2\sqrt{s_z^2}$. The relative error $\delta z = \Delta z/z$ is often used instead of the absolute one. The limiting relative error is $\delta_{\lim} z = \Delta_{\lim} z/z$.

If the confidence interval includes zero, or, which is the same, $\Delta_{\lim} z \geqslant z$ and $\delta_{\lim} z \geqslant 1$, the accuracy of the calculations is so low that the use of its results loses all meaning. The latter circumstance must be taken into consideration in thermodynamic calculations. For example, the comparatively low heats ΔH_h of the reactions of conversion of hydrocarbon fractions are sometimes calculated from the heats of combustion ΔH_c of the reactants:

$$\Delta H_h = \Delta H_{c,r} - \Delta H_{c,pr}$$

The magnitude of ΔH_h does not usually exceed 200 kJ/mol, while ΔH_c reaches 40 000 kJ/mol. Assume that ΔH_c is determined with a standard error of 100 kJ/mol. Hence, by formula (2.2), we have $s^2_{\Delta H_h} = 2s^2_{\Delta H_c} = 20\,000$, and $s_{\Delta H_h} = 145$. In this case, assuming that the probability 0.95 determines the limiting error, we have $\Delta_{\lim} z = 290$, and the confidence interval for z will be the region from $z - 290$ to $z + 290$. At values of z below 290, this interval will include zero. Consequently, the use of the heats of combustion for calculating the heats of reactions of hydrocarbons requires a very high accuracy of measuring ΔH_c (the absolute error must never exceed 10 kJ/mol).

Below are given equations for calculating the quantities s_z^2 from the values of $s_{u_i}^2$ for some specific formulas used in thermodynamic calculations. These equations were obtained on the basis of expression (2.2):

Kind of relation	Working equation	Field of application
$z = f(u_1, \ldots, u_k)$	s_z^2	Calculations of heats of reactions from heats of combustion, formation, etc. Calculations of ΔH°, ΔS°, and ΔG° for arbitrary temperature
$z = \sum_i a_i u_i$	$s_z^2 = \sum_i a_i^2 s_{u_i}^2$	
$z = \exp(-u/a)$	$s_z^2 = \frac{1}{a^2} \exp\left(-\frac{2u}{a}\right) s_u^2$	Calculation of equilibrium constant K_p° from value of ΔG°
$z = \prod_i u_i^{a_i}$	$s_z^2/z^2 = (\delta z)^2 = \sum_i (a_i \delta u_i)^2$	Calculation of K_γ from values of γ_i, etc.

Equation (2.2) also holds for implicit relations, therefore the calculation of s_z^2 requires the determination of the derivative of an implicit function. It is known that for the implicit function $\varphi(z, u) = 0$, we have

$$\frac{dz}{du} = -\frac{\partial\varphi}{\partial u} \Big/ \frac{\partial\varphi}{\partial z}$$

Similarly for a function of many variables $\varphi(z, u_1, \ldots, u_k) = 0$:

$$\frac{dz}{du_i} = -\frac{\partial\varphi}{\partial u_i} \Big/ \frac{\partial\varphi}{\partial z}$$

Hence

$$s_z^2 = \sum_i \left(\frac{dz}{du_i}\right)^2 s_{u_i}^2 = \sum_i \left[\left(\frac{\partial\varphi}{\partial u_i}\right)^2 \Big/ \left(\frac{\partial\varphi}{\partial z}\right)^2\right] s_{u_i}^2$$

and it is not difficult to estimate the calculation errors.

Let us now consider specific examples of calculating errors.

1. Calculations of the Heats of Reactions. We use data on the heats of formation $\Delta H^\circ_{f,i,298}$ and the coefficients a_i, b_i, and c_i of the equation $C^\circ_{p,i} = a_i + b_i T + c_i T^2$ for each component of the reaction mixture:

$$\Delta H^\circ_T = \left(\sum \nu_i \Delta H^\circ_{f,\,i,\,298}\right)_{pr} - \left(\sum \nu_i \Delta H^\circ_{f,\,i,\,298}\right)_r + \Delta a\,(T - 298) + \frac{\Delta b}{2}(T^2 - 298^2) + \frac{\Delta c}{3}(T^3 - 298^3)$$

In accordance with expression (2.2) and the above data, we have:

$$s^2_{\Delta H^\circ} = \sum \nu_i^2 s^2_{\Delta H^\circ_{f,\,i}} + (T - 298)^2 s^2_{\Delta a} + \left(\frac{T^2 - 298^2}{2}\right)^2 s^2_{\Delta b} + \left(\frac{T^3 - 298^3}{3}\right)^2 s^2_{\Delta c}$$

In most cases, the terms with Δa, Δb, and Δc in the equations for ΔH° and $s^2_{\Delta H^\circ}$ are small. Moreover, we can consider that all

the values of $s^2_{\Delta H^\circ_{f,i}}$ are the same: $s^2_{\Delta H^\circ_{f,i}} = s_0^2$. Consequently, when k substances react $(\sum \nu_i = 1)$, we have

$$s^2_{\Delta H^\circ} = k s_0^2, \quad s_{\Delta H^\circ} = s_0 \sqrt{k}$$

i.e. the standard absolute error of the calculations is at least $\sqrt{k}$ times larger than the absolute error in determining $\Delta H^\circ_{f,i}$.

2. Calculations of the Change in the Gibbs Energy. The quantity ΔG° is calculated from the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, where ΔH° and ΔS° are determined with the errors $s_{\Delta H^\circ}$ and $s_{\Delta S^\circ}$, while the exact value of T is given. Therefore, $s^2_{\Delta G^\circ} = s^2_{\Delta H^\circ} + T^2 s^2_{\Delta S^\circ}$.

Generally, the value of ΔS° is approximately three orders of magnitude less than that of ΔH°, and accordingly $s_{\Delta S^\circ} \leqslant s_{\Delta H^\circ}$. Therefore, at low values of T, the error in calculating ΔG° is determined by the error in the value of ΔH°. At high values of T, the contributions of ΔH° and ΔS° are approximately the same.

3. Calculation of the Equilibrium Constant K_a (or $K_p = K_a$ for an Ideal System) from the Value of ΔG°. Since $K_a = \exp(-\Delta G^\circ/RT)$, we have $s_K = (1/RT)\exp(-\Delta G^\circ/RT)\, s_{\Delta G^\circ}$ or $\delta K_a = s_{\Delta G^\circ}/RT$.

An absolute error of 1 kJ in determining ΔG° results for a temperature of 1000 K in a relative error of calculating the equilibrium constant of $\delta K = 1000/(8.31 \times 1000) = 0.12$ or 12%.

4. Calculations of the Equilibrium Degree of Conversion y from the Value of the Equilibrium Constant K_x. In a general case, we do not succeed in expressing y explicitly in terms of K_x. If we go over to the relation $\varphi(K_x, y) = K_x - f(y) = 0$, we find:

$$s_y^2 = \left(\frac{dy}{dK_x}\right)^2 s^2_{K_x} = \left[\left(\frac{\partial\varphi}{\partial K_x}\right)^2 \Big/ \left(\frac{\partial\varphi}{\partial y}\right)^2\right] s^2_{K_x} = \left[1 \Big/ \left(\frac{df(y)}{dy}\right)^2\right] s^2_{K_x}$$

or

$$s_y = s_{K_x} \Big/ \left|\frac{df(y)}{dy}\right|$$

An analysis of the latter expression reveals that the errors will be especially considerable when the value of the derivative df/dx is small; simultaneously, the value of K_x should be limited. Indeed, at large values of K_x, the degree of conversion differs insignificantly from unity, the derivative df/dx will also be significant, while the error of calculations s_y will be negligibly small.

Let us consider for purposes of illustration the estimate of the errors in calculating the degree of conversion for the reaction $A_1 + A_2 \rightarrow A_1' + A_2'$ when the initial mixture contains no reaction products and the molar ratio of A_2 to A_1 is unity. In this case, the equilibrium constant K_x is related to the degree of conversion y by the expression

$$K_x = f(y) = \frac{y^2}{(1-y)^2}$$

Hence

$$\frac{df(y)}{dy} = \frac{2y}{(1-y)^3}$$

Consequently,

$$s_y = s_{K_x} \Big/ \frac{2y}{(1-y)^3} = y\,\frac{1-y}{2}\,s_{K_x} \Big/ \frac{y^2}{(1-y)^2}$$

or

$$\frac{s_y}{y} = \frac{1-y}{2}\,\frac{s_{K_x}}{K_x}; \quad \delta y = \frac{1-y}{2}\,\delta K_x$$

If the degree of conversion is not large, then $\delta y \approx \frac{1}{2}\,\delta K_x$, i.e. the relative error of calculating the quantity y is about half of the relative error of calculating the equilibrium constant. At moderate degrees of conversion, δy diminishes; for example, for $y = 0.5$, the last equation yields $\delta y = 0.25\delta K_x$. Finally, at high degrees of conversion, i.e. at $y \to 1$, the relative error of calculating the degree of conversion is close to zero.

These conditions are observed approximately for reactions with any stoichiometric equations. One should therefore take into account that $0 \leqslant \delta y \leqslant \delta K_x \times 0.5$.

It is obvious from the above treatment that when calculating heats (ΔH), the inaccurate determination of the heats of combustion of substances (or the heats of formation calculated from them) is the main source of errors. When finding ΔG°, K_p, K_x, and y, additional errors arise because of the inaccuracy in determining the entropies.

The refinements in calorimetric techniques when burning substances enable one to measure ΔH_c° with a very high accuracy, namely, the relative error in determining ΔH_c° is usually below 0.05%; however, the magnitude of these errors is quite noticeable. The data on the heats of combustion and, consequently, on the other thermodynamic functions of substances are constantly being refined. For example, the heat of combustion of methane under standard pressure and at 298 K was considered to equal —890.31 kJ/mol in the sixties; at present, a value of —890.71 kJ/mol has been obtained for this quantity. The value previously used for *n*-butane was $\Delta H_c^\circ = -2878.38$ kJ/mol, whereas the latest measurements have yielded $\Delta H_c^\circ = -2877.54$ kJ/mol [11].

The possible errors in measuring ΔH_c° and ΔH_f° for organic compounds have been analysed in [12] (Table 6).

Examination of these data reveals that for hydrocarbons and their derivatives, the maximum error in the value of $\Delta H_{c,298}^\circ$ is mainly within the limits of 0.5 to 1.0 kJ/mol, and of $\Delta H_{f,298}^\circ$, within the limits of 0.6 to 1.1 kJ/mol.

The maximum errors with a probability of 95% can be considered equal to two standard errors, therefore we can assume that $2s_{\Delta H_f^\circ} \approx$

Table 6. **Standard Heats of Combustion, Formation, and the Maximum Errors in Their Determination for Selected Substances**

Substance in the state of an ideal gas	$-\Delta H^\circ_{c,298}$, kJ/mol	$-\Delta H^\circ_{f,298}$, kJ/mol
Methane	890.71±0.38	−74.46±0.41
Ethane	1560.69±0.25	−83.82±0.38
Propane	2219.17±0.46	−104.68±0.62
n-Butane	2877.54±0.63	−125.65±0.84
Isobutane	2869.00±0.59	−134.19±0.81
n-Pentane	3535.44±0.96	−147.09±1.18
Ethylene (ethene)	1411.18±0.29	+52.50±0.40
Propylene (propene)	2057.73±0.63	+19.71±0.75
1-Butene	2716.80±0.75	−0.56±0.93
cis-2-Butene	2709.77±1.21	−7.59±1.18
trans-2-Butene	2706.63±0.96	−10.73±1.10
1-Butyne	2596.76±0.84	+165.23±1.00
1,3-Butadiene	2540.36±0.75	+108.83±0.92
2-Methyl-1,3-butadiene	3186.62±0.96	+75.75±1.17
Cyclopropane	2091.29±0.54	+53.27±0.68
Methanol	764.08±0.17	−201.09±0.23
Ethylene oxide	1306.04±0.59	−52.64±0.65
Water	—	−285.83±0.04
Carbon monoxide	282.84±0.13	−110.67±0.18

≈ 0.8 kJ/mol. Now, taking into account that it is exactly the inaccuracies in determining ΔH°_c and ΔH°_f that are the main cause of errors in thermodynamic calculations, we can give the following estimates.

The standard error in determining the heat of a reaction (in kJ) is:

$$s_{\Delta H^\circ} = \frac{1}{2}(2s_{\Delta H^\circ}) \approx \frac{1}{2}(0.8\sqrt{k}) = 0.4\sqrt{k}$$

The standard error in determining ΔG° of a reaction (we disregard the errors in the entropy) (in kJ) is:

$$s_{\Delta G^\circ} \approx s_{\Delta H^\circ} \approx 0.4\sqrt{k}$$

The standard error in determining the equilibrium constant is:

$$s_K = \frac{s_{\Delta G^\circ}}{RT}\exp\left(-\frac{\Delta G^\circ}{RT}\right), \quad \delta K_p = \frac{s_K}{K_p} = \frac{s_{\Delta G^\circ}}{RT}$$

$$\delta K_p \approx \frac{0.4\sqrt{k}}{RT}$$

where k is the number of reactants.

It should be noted that the real error can be either somewhat larger than the cited ones owing to inaccuracies in determining the heat capacities and entropies, or somewhat lower if the actual maximum error in determining ΔH°_c is less than 0.8 kJ/mol.

Let us illustrate the order of the values of these errors using the thermodynamic calculations for the reaction *n*-butane → isobutane. The heat of this reaction ΔH° is 8.4 kJ. Assume that $2s_{\Delta H_f^\circ} = 0.8$ kJ/mol. Hence,

$$2s_{\Delta G^\circ} \approx 2s_{\Delta H^\circ} = 0.8\sqrt{2} = 1.1 \text{ kJ}$$

Therefore, $\Delta H^\circ = 8.4 \pm 1.1$ kJ.

The maximum relative error in determining the equilibrium constant for 400 K is:

$$\delta_{\max} K_p = 2\delta K_p = \frac{1100}{8.31 \times 400} = 0.3 \text{ or } 30\%$$

Taking into account that

$$y = \frac{K_p}{1+K_p}, \quad \delta_{\max} y = (1-y)\,\delta_{\max} K_p$$

and for $y = 0.6$, we have $\delta_{\max} y = 12\%$.

Thus, the calculations of the degree of conversion enable us to find this quantity with a maximum error of 12%, i.e. $y = 0.6 \pm 0.07$.

With such a maximum error, we obviously cannot speak of deviation from thermodynamic equilibrium at $y = 0.53$ or $y = 0.67$.

It should be noted that the considered situation characterizes high relative errors (owing to the high value of the ratio $s_{\Delta H^\circ}/\Delta H^\circ$). In most real cases, the relative errors will be smaller, but they nevertheless remain significant, and their estimation is desirable.

2.2. Reactions in an Ideal Gas Mixture

If each component of a mixture and the mixture as a whole obey the laws of ideal gases, thermodynamic calculations are the simplest.

The heats of reactions ΔU (at v = const) and ΔH (at p = const) do not depend on the volume or pressure of the system, but do depend on the temperature. If v_0 and v are the reaction volumes, while p_0 and p are the pressures in the system, we have $\Delta U^{v_0} = \Delta U^v$ and $\Delta H^{p_0} = \Delta H^p$ when $v_0 \neq v$ and $p_0 \neq p$.

For a reaction, we have

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta C_p \, dT \tag{2.3}$$

Since $\Delta H_T = \Delta U_T + p\Delta v$, while for the conversion of stoichiometric amounts of the reactants we have $p\Delta v = (\sum \nu_i) RT$, then

$$\Delta H_T = \Delta U_T + (\sum \nu_i) RT \tag{2.4}$$

where $\sum \nu_i$ is the change in the number of moles in a reaction.

We can thus use tabulated data to calculate ΔH and then, if necessary, find ΔU from Eq. (2.4).

The quantities ΔS and ΔG depend on the pressure. The relations of thermodynamics for T = const yield

$$\left(\frac{\partial S}{\partial p}\right)_T = -\frac{v}{T}, \quad \left(\frac{\partial \Delta S}{\partial p}\right)_T = -\frac{\Delta v}{T} = -\left(\sum \nu_i\right)\frac{R}{p}$$

i.e., when a reaction is conducted at the pressures p and p_0:

$$\Delta S^p = \Delta S^{p_0} - \int_{p_0}^{p} \sum \nu_i \frac{R}{p}\, dp = \Delta S^{p_0} - \left(\sum \nu_i\right) R \ln \frac{p}{p_0}$$

Moreover,

$$\left(\frac{\partial G}{\partial p}\right)_T = v, \quad \left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta v = \left(\sum \nu_i\right)\frac{RT}{p}$$

Consequently,

$$\Delta G^p = \Delta G^{p_0} + \int_{p_0}^{p} \left(\sum \nu_i\right) RT\, d \ln p = \Delta G^{p_0} + \left(\sum \nu_i\right) RT \ln \frac{p}{p_0}$$

If standard thermodynamic tables are used, then after performing the relevant calculations for the standard pressure $p°$ (i.e. $p_0 = p°$), we can recalculate ΔS^p and ΔG^p for any other pressure by the above relations.

Calculations based on the data of standard thermodynamic tables enable us to determine the quantity $\Delta G°$. It does not depend on the pressure. Knowing this quantity, we can easily find $K_p^\circ = \exp(-\Delta G°/RT)$, $K_p = K_p^\circ (p°)^{\sum \nu_i}$, or $K_c = K_p (RT)^{-\sum \nu_i}$, or $K_x = K_p p^{-\sum \nu_i}$.

We shall illustrate how these calculations are performed using the reaction of dehydrogenation of cyclohexane to benzene ($C_6H_{12} \rightarrow C_6H_6 + 3H_2$) at 300 and 800 K; the reaction mixture can be considered as an ideal gas.

From thermodynamic tables (see Tables A.21 and A.19 in Appendix 2, we find the thermodynamic functions of the reactants in the state of an ideal gas at standard pressure. Their values are given in Table 7.

Table 7. **Thermodynamic Functions for Reaction $C_6H_{12} \rightarrow C_6H_6$ at 300 and 800 K**

Substance	300 K		800 K	
	ΔH_f°, kJ/mol	$S°$, J/(mol·K)	ΔH, kJ/mol	$S°$, J/(mol·K)
Cyclohexane	—123.34	298.90	—155.60	448.05
Benzene	82.80	269.74	64.89	402.12
Hydrogen	0	130.76	0	159.44

A. Heats of the reaction:

$$\Delta H^\circ_{300} = 82.80 - (-123.34) = 206.14 \text{ kJ/mol}$$

$$\Delta H^\circ_{300} = 64.89 - (-155.60) = 220.49 \text{ kJ/mol}$$

It should be noted that since data are available on the heats of formation at various temperatures, there is no need to directly apply Kirchhoff's formulas.

If a reaction is conducted in a closed vessel of constant volume, its heat is determined by the change in the internal energy. For the reaction being considered,

$$\Delta U = \Delta H - 3RT$$

We find

$$U_{300} = 206.14 - 3 \times 8.31 \times 10^{-3} \times 300 = 198.66 \text{ kJ}$$

$$\Delta U_{800} = 220.49 - 3 \times 8.31 \times 10^{-3} \times 800 = 200.55 \text{ kJ}$$

It should be noted that ΔH does not depend on the pressure, and ΔU on the volume.

B. Entropies of the reaction:

$$\Delta S^\circ_{800} = 269.74 + 3 \times 130.76 - 298.90 = 363.12 \text{ J/K}$$

$$\Delta S^\circ_{800} = 402.12 + 3 \times 159.44 - 448.05 = 432.39 \text{ J/K}$$

At 5 MPa and 800 K, we have

$$\Delta S^5_{800} = \Delta S^\circ_{800} - 3R \ln (5/0.1) = 432.39 - 97.5 = 334.89 \text{ J/K}$$

C. Gibbs energies of the reaction;

$$\Delta G^\circ_{300} = \Delta H^\circ_{300} - 300\Delta S^\circ_{300} = 206.14 - 300 \times 363.12 \times 10^{-3} = 97.20 \text{ kJ}$$

$$\Delta G^\circ_{300} = 220.49 - 800 \times 432.39 \times 10^{-3} = -125.42 \text{ kJ}$$

We see that the dehydrogenation of cyclohexane in the gas phase is possible thermodynamically only at elevated temperatures ($\Delta G < 0$).

D. Equilibrium constants:

$$K^\circ_{p,300} = \exp\left(-\frac{\Delta G^\circ_{300}}{R \times 300}\right) = \exp\left(-\frac{97.20}{8.31 \times 10^{-3} \times 300}\right) = \exp(-39) \approx 0$$

$$K^\circ_{p,800} = \exp\left(\frac{125.42}{8.31 \times 10^{-3} \times 800}\right) = \exp(18.9)$$

The values of K°_p show that dehydrogenation in the gas phase will not proceed at 300 K and will proceed virtually completely at 800 K.

The values of K°_p do not depend on the pressure.

It was shown on a previous page that $K_p = K^\circ_p (p^\circ)^3$ and $K_x = K^\circ_p (p^\circ/p)^3$, where p° is the standard pressure, and p is the pressure at which the reaction is conducted. Therefore, $K_{p,300} = \exp(-30.7)\ (0.1)^3$ MPa, and $K_{p,800} = \exp(18.9)\ (0.1)^3$ MPa.

At 800 K and 0.1 MPa, we have $K_x = \exp(18.9)$; at 800 K and 5 MPa, we have $K_x = \exp(18.9)\ (1/50)^3 = \exp(7.1)$. A growth in the pressure appreciably lowers the value of K_x.

E. Equilibrium Composition. If the initial mixture contains no reaction products, expression (1.76) for the reaction being considered yields the following relation between K_x and the equilibrium degree of conversion y:

$$K_x = \frac{27y^4}{(1-y)(1+3y)^3}$$

At 300 K, both K_x and y are close to zero. At 800 K and pressures of 0.1 MPa or 5 MPa, $y < 0.99$ corresponds to the values of K_x, i.e. the reaction is practically irreversible.

It should be noted that at temperatures lower than 800 K, the value of K_x will be limited, and the value of y will appreciably differ both from zero and from unity.

2.3. Reactions in a Real Gas Mixture

The laws of ideal gases become less accurate for real gas mixtures when such a mixture approaches the critical point, i.e. when the pressure of the mixture is higher and its temperature is lower.

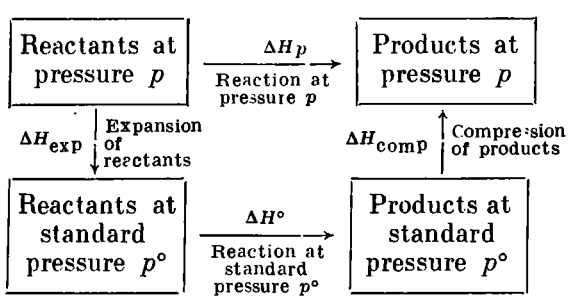
A. Temperature Dependence of Heat of Reaction. For any systems (see Table 1), the relations $(\partial H/\partial T)_p = C_p$ and $(\partial \Delta H/\partial T)_p = \Delta C_p$ hold. Therefore, the equation $\Delta H^\circ = f(T)$ at p = const can also be used for reactions of real gases [see Eq. (2.3)].

B. The pressure dependence of the heat of a reaction is determined by the equation (see Table 1):

$$\left(\frac{\partial \Delta H}{\partial p}\right)_T = \Delta (h_p + v) \tag{2.5}$$

In accordance with the above treatment, the heat (enthalpy) of a reaction ΔH_p at the pressure p is determined from the heat of the reaction ΔH° at standard temperature and the heats ΔH_{exp} of expansion of the reactants and ΔH_{comp} of compression of the products.

In accordance with the scheme:



$$\Delta H_p = \Delta H_{exp} + \Delta H^\circ + \Delta H_{comp}$$

For a reaction in the real gas phase, ΔH° is practically the same as for a reaction in the ideal gas phase, and it can be found from the heats of formation or combustion of the reactants in the state of an ideal gas. The calculations of ΔH_{exp} and ΔH_{comp} have been treated on an earlier page (p. 66).

Here the following circumstance must be taken into consideration. Although a reaction is conducted at the pressures p° (atmospheric)

and p (increased), these pressures are the sum of the partial pressures p_i of the reactants (prior to the reaction) or products p_i' (after the reaction). Assume that $p_i = \alpha_i p$ and $p_i' = \alpha_i' p$. Therefore the pressure of a component in accordance with the above scheme should change from zero to $\alpha_i p$. In specific calculations, it is considered that α is close to the mole fraction of a component, i.e. for the reactants $\alpha_i = \nu_i/(\nu_1 + \nu_2 + \ldots)$, for the products $\alpha_i' = \nu_i'/(\nu_1' + \nu_2' + \ldots)$, or, even taking into account the slight influence of the pressure, $p_i \approx p$ and $p_i' \approx p$.

It should be noted that for most reactions the pressure only slightly affects the heat of a reaction.

C. The pressure dependence of ΔS and ΔG is as follows (see Table 2):

$$\left(\frac{\partial \Delta S}{\partial p}\right)_T = \frac{\Delta h_p}{T}, \quad \left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta v$$

Since

$$h = -T\left(\frac{\partial v}{\partial T}\right)_p \text{ and } \Delta h_p = -T\left(\frac{\partial \Delta v}{\partial T}\right)_p$$

we have

$$\left(\frac{\partial \Delta S}{\partial p}\right)_T = -\left(\frac{\partial \Delta v}{\partial T}\right)_p$$

$$\Delta G^p = \Delta G^{p_0} + \int_{p_0}^{p} \Delta v\, dp, \quad \Delta S^p = \Delta S^{p_0} - \int_{p_0}^{p} \left(\frac{\partial \Delta v}{\partial T}\right)_p dp$$

Integration can be performed by using the values of the compression factors Z_i of the components and the equation of state for one mole in the form of $pv = ZRT$. Hence,

$$\Delta v = \Delta Z \frac{RT}{p}, \quad \left(\frac{\partial \Delta v}{\partial T}\right)_p = \Delta Z \frac{R}{p} + \frac{RT}{p}\left(\frac{\partial \Delta Z}{\partial T}\right)_p$$

Consequently,

$$\Delta G^p = \Delta G^{p_0} = RT \int_{p_0}^{p} \Delta Z\, d \ln p,$$

$$\Delta S^p = \Delta S^{p_0} - R \int_{p_0}^{p} \Delta Z\, d \ln p - RT \int_{p_0}^{p} \left(\frac{\partial \Delta Z}{\partial T}\right)_p d \ln p$$

In these expressions

$$\Delta Z \equiv \sum \nu_i Z_i = \left(\sum \nu_i Z_i\right)_{pr} - \left(\sum \nu_i Z_i\right)_r$$

For integration, it is convenient to use the general relation $Z = Z(\tau, \pi, Z_{cr})$ for a real gas.

The quantity ΔS_p is calculated by the same scheme as ΔH_p with the use of tables or graphs expressing the difference between the

entropies of a real and ideal gas as a function of the reduced parameters τ and π (see Fig. 10). The value of ΔG_p is usually found from those of ΔH_p and ΔS_p, namely,

$$\Delta G_p = \Delta H_p - T\Delta S_p$$

Thus, the scheme of calculating ΔG_p for a reaction in a real gas mixture is as follows: (1) calculation of ΔH° and ΔS° for a reaction in an ideal gas mixture; (2) calculation of ΔH_p and ΔS_p for a reaction in a real gas mixture; (3) calculation of ΔG_p from the values of ΔH_p and ΔS_p.

The sign of ΔG is used to establish the thermodynamic probability of a reaction.

In many cases, however, the possible extent of a reaction is directly established from the value of $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ without resorting to calculations of ΔG_p. The explanation is that it is the simplest to use thermodynamic tables, which give the properties of substances in the state of an ideal gas, to determine ΔG°.

D. Equilibrium Constants. A reaction in a real gas mixture is characterized by the equilibrium constant K_f [see Eq. (1.32)] and Eq. (1.39) of an isotherm. Expression (1.65) can be used for the fugacity of a component.

If a reaction is conducted so that the reactants and products are in the standard state of an ideal gas, the value of ΔG° is found from tabulated thermodynamic functions, and in this case

$$\Delta G^\circ = -RT \ln K_p^\circ$$

The use of the fugacities instead of the partial pressures and the constant K_f instead of K_p for a real gas mixture results in the fact that we succeed in determining K_f instead of K_p from the value of K_p°. Since by Eq. (1.65) we can write K_f in the form

$$K_f = K_\gamma K_x p^{\sum \nu_i}$$

then the mentioned expressions yield

$$K_x = \frac{K_p^\circ}{K_\gamma} \left(\frac{p^\circ}{p}\right)^{\sum \nu_i}$$

Knowing K_x, we can evaluate the equilibrium degree of conversion y as for an ideal gas [see Eq. (1.76)] because the expressions relating K_x and y do not depend on the physical properties of the components.

Thus, the main problem in calculating K_x and y for a real gas mixture is the determination of the fugacity (activity) coefficients γ_i, and from them the value of K_γ. It should be noted that the coefficient γ_i for a mixture component at the pressure p and temperature T, generally speaking, does not equal the coefficient γ_i° of an individual gas at the same pressure and temperature in the same way as

the fugacities of a component in a mixture f_i and in the pure gas f_i° are not equal. If, however, the partial molar volume of a component at the temperature and pressure of a mixture equals the molar volume of the same individual gas at the same temperature and pressure, condition (1.65) will be satisfied for the fugacity, and therefore $\gamma_i^\circ = \gamma_i$. With such an approximation (and it is used in calculations), the determination of K_x and y is quite simple and includes the following steps:

(1) calculation of the quantities ΔG° and K_p° from the data of standard thermodynamic tables;

(2) calculation of γ_i° for each component of the reaction mixture provided that it is at the pressure and temperature of the reaction mixture; calculation of the quantity K_{γ°;

(3) calculation of the constant K_x from the condition $K_p = K_{\gamma^\circ} K_x (p/p^\circ)^{\sum \nu_i}$; determination of the equilibrium degree of conversion y from the value of K_x and relation (1.76).

It should be noted that calculations of the equilibrium of reactions in an atmosphere of hydrogen [9] have shown that such a procedure yields values of K_x with a satisfactory accuracy (the calculated and experimental values of K_x were compared) up to pressures of 40-50 MPa.

Let us take as an example the thermodynamic calculations of the reaction of dehydrogenation of cyclohexane to benzene in the gas phase at 800 K and 5 MPa considered above (p. 80), having in view that the laws of ideal gases may not be observed.

A. Heat of Reaction. Taking into account the changes in the enthalpy when the reactants expand and the products are compressed, we have:

$$\Delta H_{800}^5 = \Delta H_{\text{exp}}\,(C_6H_{12}) + \Delta H_{800}^\circ + \Delta H_{\text{comp}}\,(C_6H_6) + 3\Delta H_{\text{comp}}\,(H_2)$$

The value of ΔH_{800}° has been determined earlier (220.49 kJ/mol), while the calculation of ΔH_{exp} and ΔH_{comp} was described on p. 66.

The data needed for these calculations are given in Table 8.

Table 8. **Data for Calculating ΔH_{800}^5 for the Reaction $C_6H_{12} \rightarrow C_6H_6$**

Substance	p_{cr}, MPa	T_{cr}, K	π	τ	$\Delta H_{comp}/T_{cr}$, J/(mol·K)	$\Delta H_{exp}/T_{cr}$, J/(mol·K)
Cyclohexane	4.0	554	1.25	1.50	—	4.94
Benzene	4.8	562	1.03	1.42	—4.60	—
Hydrogen	1.3	19.4	2.40	24.1	≈ 0	≈ 0

Using the above formula and the data of Table 8, we find:

$$\Delta H_{800}^5 = 4.94 \times 10^{-3} \times 554 + 220.49 - 4.60 \times 10^{-3} \times 562 = 220.64 \text{ kJ}$$

The pressure can be seen to have no substantial effect on the heat of the reaction.

Let us sum the obtained data to illustrate the influence of various factors on the heat of the reaction of dehydrogenation of cyclohexane to benzene in the gas phase:

Temperature, K	300	800	800
Pressure, MPa	0.1	0.1	5
Heat of the reaction (in kJ):			
at constant pressure	206.14	220.49	220.64
at constant volume	198.66	—	—

B. The calculation of ΔG°_{800} for a real system requires the finding of ΔS°_{800} by the same scheme as the calculation of the enthalpy:

$$\Delta S^{\circ}_{800} = \Delta S_{\text{exp}}(C_6H_{12}) + \Delta S^{\circ}_{800} + \Delta S_{\text{comp}}(C_6H_6) + 3\Delta S_{\text{comp}}(H_2)$$

The value of ΔS°_{800} has been determined on a previous page (432.39 J/K). By Fig. 10, we find $\Delta S_{\text{exp}}(C_6H_{12}) = +3$ J/K, $\Delta S_{\text{comp}}(C_6H_6) = -2$ J/K, and $3\Delta S_{\text{comp}}(H_2) \approx 0$. Consequently,

$$\Delta S^{\circ}_{800} = 3 + 432.39 - 2 = 433.39 \text{ J/K}$$

C. The Gibbs energy of the reaction:

$$\Delta G^{\circ}_{800} = \Delta H^{\circ}_{800} - 800\ \Delta S^{\circ}_{800} = 220.64 - 800 \times 433.39 \times 10^{-3}$$
$$= -126.07 \text{ kJ}$$

This value is virtually the same as for an ideal gas mixture. It is used for determining the thermodynamic probability of a reaction, but not for calculating the equilibrium constant and the equilibrium composition.

D. Equilibrium constants. The standard equilibrium constant $K^{\circ}_p = \exp(-\Delta G^{\circ}/RT)$ and at 800 K it is $\exp[125.42/(8.31 \times 10^3 \times 800)] = \exp(18.9)$.

We find the values of γ°_i for the components from Fig. 4. They are $\gamma^{\circ}(C_6H_{12}) = 0.80$, $\gamma^{\circ}(C_6H_6) = 0.87$, and $\gamma^{\circ}(H_2) = 1$. Hence,

$$K_{\gamma^{\circ}} = \frac{0.87 \times 1^3}{0.81} = 1.07$$

$$K_x = \frac{K^{\circ}_p}{K_{\gamma^{\circ}}} \left(\frac{p^{\circ}}{p}\right)^3 = e^7$$

For an ideal gas mixture, $K_x = e^{7.1}$. The taking into account of the properties of a real and ideal gases in this example changes the value of K_x negligibly.

E. The equilibrium composition is calculated from the value of K_x in the same way as for an ideal gas because Eq. (1.76) relating K_x and y holds for any systems.

2.4. Reactions in an Ideal Solution

A solution is considered to be ideal when Raoult's law is obeyed for each of its components:

$$p_i = p^{\circ}_i x^{\text{lq}}_i$$

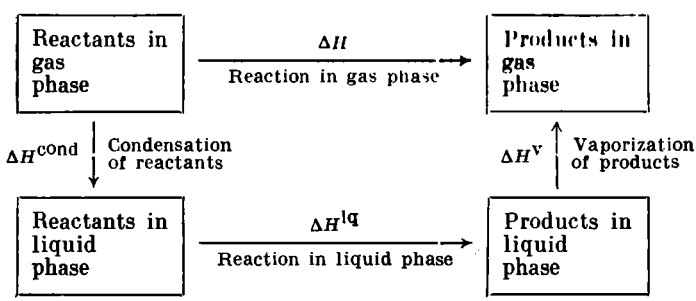
where p_i and p°_i are the pressures of the saturated vapour of the i-th component over the solution and the pure component, respectively, and x^{lq}_i is the mole fraction of the i-th component in the liquid phase.

It is also assumed that the laws of an ideal gas are observed in the gas phase. The heats, equilibrium constants, and equilibrium compositions can be calculated for reactions in solutions by using the thermodynamic quantities given in standard thermodynamic tables for the reactions both in the liquid and the gas state. For this reason, we consider below, particularly, the relation between the thermodynamic quantities for the same reaction performed at constant temperature in the liquid or gas phases.

A. Reactions in a solution generally proceed without an appreciable change in the volume ($\Delta v^{lq} \approx 0$). Hence, $\Delta H^{lq} = \Delta U^{lq} + p\Delta v^{lq} \approx \Delta U^{lq}$, and the values of the heats of reactions at constant pressure (ΔH^{lq}) and volume (ΔU^{lq}) virtually coincide. For the same reason, the changes in the Gibbs and Helmholtz energies coincide.

B. The heats of a reaction are calculated on the basis of Hess's law from the heats of formation or combustion of the components in the liquid phase.

The heat of a reaction ΔH^{lq} in a liquid phase can also be determined from the heat of the same reaction in the gas phase by the scheme for an isobaric-isothermal process:



Since $\Delta H = \Delta H^{cond} + \Delta H^{lq} + \Delta H^{v}$, the value of ΔH^{lq} can be found from the heat of a reaction ΔH in the gas phase, and also from the heats of condensation of stoichiometric amounts of the reactants ΔH^{cond} and vaporization of stoichiometric amounts of the products ΔH^{v}.

The temperature dependence of the heat of a reaction is determined by Kirchhoff's law:

$$\Delta H_T^{lq} = \Delta H_{T_0}^{lq} + \int_{T_0}^{T} \Delta G_p^{lq}\, dT \qquad (2.6)$$

Therefore ΔH_T^{lq} is calculated in the same way as for reactions in the gas phase (see above). The pressure does not practically affect the heat of a reaction in the liquid phase because it follows from the

conditions

$$\left(\frac{\partial \Delta H^{lq}}{\partial p}\right)_T = -T\left(\frac{\partial \Delta v^{lq}}{\partial T}\right)_p + \Delta v^{lq} \text{ and } \Delta v^{lq} \approx 0$$

that

$$\left(\frac{\partial \Delta H^{lq}}{\partial p}\right)_T \approx 0$$

C. The change in the Gibbs energy can be calculated for the transformation of stoichiometric amounts of the components by an equation holding for any phases, namely, $\Delta G^{lq} = \Delta(\nu_i \mu_i^{lq})$. If, however, a reaction is conducted in a "large" system (the concentrations of the components during the reaction of small amounts of the substances do not virtually change) and the system is in equilibrium (an infinitely slow reaction), phase equilibrium sets in at which the chemical potential of a component in the liquid (μ_i^{lq}) and vapour (μ_i) phases is the same: $\mu_i^{lq} = \mu_i$. Consequently, the change in the Gibbs energy for the transformation of stoichiometric amounts of substances in the liquid (ΔG^{lq}) and vapour (gas) phases (ΔG) is the same:

$$\Delta G^{lq} = \Delta(\nu_i \mu_i^{lq}) = \Delta(\nu_i \mu_i) = \Delta G$$

D. The calculation of the equilibrium constants and equilibrium compositions is based on the use of an equation relating the chemical potential to the composition of the liquid phase. It is the simplest to obtain such an equation by taking into account that for the gas phase

$$\mu_i = RT \ln p_i + r_i(T)$$

and in phase equilibrium

$$\mu_i^{lq} = \mu_i = RT \ln p_i + r_i(T)$$

where p_i is the saturated vapour pressure of the i-th component over the solution, and r_i is an arbitrary function of the temperature.

The general condition of chemical equilibrium at T, v or T, p = = const holding for reactions in any systems has the form (see above) $\Delta(\nu_i \mu_i) = 0$. For an equilibrium mixture of reaction components in an ideal solution, this condition yields

$$K_p = \frac{\prod\limits_{i'} p_i'^{\nu_i'}}{\prod\limits_{i} p_i^{\nu_i}} = \exp\left(-\Delta \frac{\nu_i r_i}{RT}\right), \quad K_p = K_p(T)$$

But, with a view to Raoult's law, we have

$$K_p = \frac{\prod\limits_{i'} (x_i'^{lq})^{\nu_i'} \prod\limits_{i'} (p_i^{\circ\prime})^{\nu_i'}}{\prod\limits_{i} (x_i^{lq})^{\nu_i} \prod\limits_{i} (p_i^{\circ})^{\nu_i}} = K_{x^{lq}} K_{p^\circ} \tag{2.7}$$

Equation (2.7) signifies that we can find the equilibrium constant $K_{x^{lq}}$ for a reaction in the liquid phase from the constant K_p for a reaction in the gas phase. To do this, we have to calculate the value of K_{p° from the saturated vapour pressures p_i° known for each component: $K_{p^\circ} = \prod_{i'} (p_i^{\circ\prime})^{\nu_i'} / \prod_i (p_i^0)^{\nu_i}$.

Consequently, the calculation of the equilibrium of a reaction in an ideal solution includes the following steps:

(1) calculation of the equilibrium constant for the same reaction in the gas phase proceeding at the same temperature and pressure;

(2) calculation of the saturated vapour pressures for each pure component and of the value of K_{p°;

(3) calculation of the equilibrium constant $K_{x^{lq}}$ for a reaction in the liquid phase, and from it the equilibrium degree of conversion y. Here one can use Eq. (1.76) because it holds for any systems.

E. The calculations of ΔG, $K_{x^{lq}}$, and y for reactions in an ideal solution can also be performed on the basis of thermodynamic properties of substances for the liquid-phase state. Since the saturated vapour pressure of a pure component $p_i^\circ = p_i^\circ(T)$ and $p_i = p_i^\circ x_i^{lq}$, we have

$$\mu_i^{lq} = RT \ln p_i + r_i(T) = RT \ln x_i^{lq} + r_i'(T)$$

where

$$r_i'(T) = RT \ln p_i^\circ + r_i(T)$$

Now from the condition of equilibrium $\Delta(\nu_i \mu_i^{lq}) = 0$, we find

$$K_{x^{lq}} = \frac{\prod_{i'} (x_i'^{lq})^{\nu_i'}}{\prod_i (x_i^{lq})^{\nu_i}} = \exp\left(-\Delta \frac{\nu_i r_i'}{RT}\right); \quad K_{x^{lq}} = K_{x^{lq}}(T)$$

The equation of an isotherm for a reaction in the liquid phase follows from the condition $\Delta G^{lq} = \Delta(\nu_i \mu_i^{lq})$ and has the form:

$$\Delta G^{lq} = RT \left[\ln \frac{\prod_{i'} (x_{i,0}'^{lq})^{\nu_i'}}{\prod_i (x_i^{lq})^{\nu_i}} - \ln K_{x^{lq}} \right] \tag{2.8}$$

Here $x_{i,0}^{lq}$ is the mole fraction of the i-th component in the solution prior to the beginning of the reaction.

F. We shall give expressions relating the equilibrium compositions for a reaction proceeding at the same temperature in the gas and liquid phases. Let p be the pressure in the gas phase, and x_i and x_i^{lq} — the mole fractions of the i-th component in the vapour and liquid.

Since

$$x_i^{lq} = \frac{p_i}{p_i^\circ} = \frac{p_i}{p} \cdot \frac{p}{p_i^\circ} = x_i \frac{p}{p_i^\circ} = x_i \frac{\sum_i x_i^{lq} p_i^\circ}{p_i^\circ}$$

we have

$$x_i = \frac{x_i^{lq} p_i^\circ}{\sum_i x_i^{lq} p_i^\circ}, \quad \sum_i x_i^{lq} = \sum_i x_i = 1 \tag{2.9}$$

If x_i and p_i° are given, solution of the system of equations (2.9) enables one to find x_i^{lq}. It should be noted that for solving system (2.9) it is convenient to write it in the form

$$x_i^{lq} = x_1^{lq} \frac{x_i p_i^\circ}{x_1 p_i^\circ}, \quad \sum_i x_i^{lq} = 1 \tag{2.10}$$

Here the subscript "1" stands for one of the mixture components.

For example, the saturated vapour pressures at 300 K of *n*-pentane $p_n^\circ = 0.068$ MPa and of isopentane $p_{iso}^\circ = 0.092$ MPa; the equilibrium constant of the reaction of their isomerization (n-$C_5H_{12} \rightarrow$ *iso*-C_5H_{12}) at the same temperature is $K_p = K_x = 13$. The content of the components, if the reaction proceeds in the gas phase, is

$$x_n = \frac{1}{1+K_x} = 0.07, \quad x_{iso} = \frac{K_x}{1+K_x} = 0.93$$

Let us determine the composition of the liquid phase if isomerization is carried out in an ideal solution.

From the system of equations (2.10), we have

$$x_n^{lq} + x_{iso}^{lq} = 1$$

$$x_{iso}^{lq} = x_n^{lq} (x_{iso} p_n^\circ + x_n p_{iso}^\circ)$$

or

$$x_n^{lq} = 1 \Big/ \left(1 + \frac{x_{iso} p_n^\circ}{x_n p_{iso}^\circ}\right) = 1 \Big/ \left(1 + \frac{0.93 \times 0.068}{0.07 \times 0.092}\right) = 0.10, \quad x_{iso}^{lq} = 0.90$$

In comparison with the vapour phase, the liquid one is lean in isopentane because it has a higher saturated vapour pressure.

If the composition of the liquid-phase reaction is calculated from the value of K_p° found from the properties of the components in the state of an ideal gas, an iteration process may be needed because we do not know the pressure p in the system at which phase equilibrium sets in. In the first iteration for the reaction temperature T and the chosen total pressure $p^{(1)}$, we find the equilibrium partial pressures $p_i^{(1)}$ of the gas-phase reaction components; next from them and the saturated vapour pressures p_i° of the components we find the mole fractions of the components in an equilibrium solution formed when the reaction is conducted in the liquid phase: $x_i^{lq(1)} = p_i^{(1)}/p_i^0$. If $\sum x_i^{lq(1)} \neq$

$\neq 1$, we go over to the second iteration at a new total pressure in the system, namely, $p^{(2)} = p^{(1)} + \Delta p$. One must have in view that $\Delta p < 0$ when $\sum x_i^{\mathrm{lq}(1)} > 1$ and, conversely, $\Delta p < 0$ when $\sum x_i^{\mathrm{lq}(1)} < 1$.

Let us illustrate these calculations for the reaction $A_1 + A_2 \rightarrow A'$. Assume that at the temperature of the reaction and with its proceeding in the gas phase, we have $K_p^\circ = 8$, $p_{A_1}^\circ = p_{A_2}^\circ = 2p^\circ$, $p_{A'}^\circ = p^\circ$, the initial mixture contains no product, and for each mole of A_1 there is one mole of A_2. For the indicated reaction

$$K_x = K_p^\circ \frac{p}{p^\circ}, \quad y = 1 - \sqrt{\frac{1}{K_x + 1}}$$

$$p_{A_1} = p_{A_2} = \frac{1-y}{2-y}\, p, \quad p_{A'} = \frac{y}{2-y}\, p$$

We assume that $p^{(1)} = 2p^\circ$. Hence $K_x^{(1)} = 16$ and $y^{(1)} = 0.76$. We find

$$p_{A_1}^{(1)} = p_{A_2}^{(1)} = \frac{0.24}{1.24}\, p = \frac{0.48}{1.24}\, p^\circ, \quad p_{A'}^{(1)} = \frac{0.76}{1.24}\, p = \frac{1.52}{1.24}\, p^\circ$$

Consequently,

$$2x_{A_1}^{\mathrm{lq}\,(1)} = 2x_{A_2}^{\mathrm{lq}\,(1)} = 2\,\frac{p_{A_1}^{(1)}}{p_{A_1}^\circ} = 0.39, \quad x_{A'}^{\mathrm{lq}\,(1)} = 1.22$$

$$\sum x_i^{\mathrm{lq}\,(1)} = 1.61 > 1$$

(The sum of all the mole fractions in the system should equal unity.) We go over to a second iteration, lowering the pressure in the system. We assume that $\Delta p = -1p^\circ$, and hence $p^{(2)} = p^\circ$. We find $K_x^{(2)} = 8$ and $y^{(2)} = 0.66$. In this case,

$$p_{A_1}^{(2)} = p_{A_2}^{(2)} = \frac{0.33}{1.33}\, p^\circ, \quad p_{A'}^{(2)} = \frac{0.66}{1.33}\, p^\circ$$

$$2x_{A_1}^{\mathrm{lq}\,(2)} = 2x_{A_2}^{\mathrm{lq}\,(2)} = 0.25, \quad x_{A'}^{\mathrm{lq}\,(2)} = 0.5 \text{ and } \sum x_i^{\mathrm{lq}\,(2)} = 0.75 < 1$$

In the second iteration, we have again obtained an incorrect result (we have undershot). Let us choose for the third iteration $\Delta p = +0.5$ and $p^{(3)} = 1.5p^\circ$. Hence $K_x^{(3)} = 12$, $y^{(3)} = 0.72$, $p_{A_1}^{(3)} = p_{A_2}^{(3)} = (0.28/1.28) \times 1.5p^\circ = 0.33p^\circ$, $p_{A'}^{(3)} = (0.72/1.72) \times 1.5p^\circ = 0.84p^\circ$, $2x_{A_1}^{\mathrm{lq}\,(3)} = 2x_{A_2}^{\mathrm{lq}\,(3)} = 0.42$, $x_{A'}^{\mathrm{lq}\,(3)} = 0.84$, and $\sum x_i^{\mathrm{lq}\,(3)} = 1.32 > 1$. For the fourth iteration, we choose $\Delta p = -0.25p^\circ$. Here $K_x^{(4)} = 10$, $y^{(4)} = 0.70$, $p_{A_1}^{(4)} = p_{A_2}^{(4)} = 0.29p^\circ$, $p_{A'}^{(4)} = 0.67p^\circ$, $2x_{A_1}^{\mathrm{lq}\,(4)} = 2x_{A_2}^{\mathrm{lq}\,(4)} = 0.29$, $x_{A'}^{\mathrm{lq}\,(4)} = 0.67$, and $\sum x_i^{\mathrm{lq}\,(4)} = 0.96 \approx 1$. Thus, resorting to rounding off, we establish that equilibrium in the liquid phase at the given temperature sets in at a reactant content (in mole fractions) of 0.15 each, a product content of 0.70, and a vapour pressure over the equilibrium liquid phase close to 1.5 of standard pressure.

It is easy to programme such an iteration process, and computerized calculations involve no difficulties.

2.5. Reactions in a Real Solution

If Raoult's law $p_i = p_i^\circ x_i^{lq}$ is not observed for the components of a solution, the latter is said to be non-ideal. In practice, solutions are not ideal whenever their components belong to different groups of substances, namely, water-alcohol, alcohol-hydrocarbon, and so on.

For reactions in real solutions, the heats ΔH, entropy increments ΔS, and Gibbs energy ΔG can be calculated in the same way as for ideal solutions or gas systems (see above) because the expressions for calculating ΔH, ΔS, and ΔG are obtained without using Raoult's law. It should be stressed that for real solutions too, ΔH, ΔS, and ΔG can be determined from the thermodynamic quantities for the components of the reacting mixture both for a gas and liquid state. The following conditions hold for real solutions.

A. The heats of reactions conducted at a constant pressure (ΔH^{lq}) or constant volume (ΔU^{lq}) are close: $\Delta H^{lq} \approx \Delta U^{lq}$.

B. The heat of a reaction ΔH^{lq} in a liquid phase can be found from the heat of the same reaction ΔH in the gas phase, the heat of condensation ΔH^{cond} of the reactants, and the heat of vaporization ΔH^{v} of the products: $\Delta H^{lq} = \Delta H - \Delta H^{cond} - \Delta H^{v}$.

C. The temperature dependence of the heat of a reaction is determined by Kirchhoff's equation (2.6). The heat of a reaction depends only slightly on the pressure.

D. The changes in the Gibbs energy ΔG^{lq} and Helmholtz energy ΔA^{lq} for reactions in the liquid phase practically coincide: $\Delta G^{lq} \approx \approx \Delta A^{lq}$.

The relation $\Delta G^{lq} = \Delta(\nu_i \mu_i^{lq})$ holds for any phases including the liquid one. Since it is presumed that phase equilibrium has time to set in during a reaction and that the chemical potentials of the components μ_i^{lq} in the liquid phase and μ_i in the gas phase are equal, we have

$$\Delta G^{lq} = \Delta(\nu_i \mu_i^{lq}) = \Delta(\nu_i \mu_i) = \Delta G$$

Consequently, ΔG^{lq} can be calculated from data on the thermodynamic properties of the components in both the liquid and gas states.

When calculating the equilibrium constants and equilibrium compositions, on the other hand, one has to obtain the equation of the chemical potential for a component of a real solution.

Since for the i-th component in a real gas mixture, we have

$$\mu_i = RT \ln f_i + r_i(T)$$

then

$$\mu_i^{lq} = \mu_i = RT \ln f_i + r_i(T) \tag{2.11}$$

This equation is not convenient because it does not relate the chemical potential to the composition of the liquid phase. Using the analogy with an ideal solution for which $\mu_i^{lq} = RT \ln x_i^{lq} + r_i'(T)$, we shall assume that for a real solution we can use a similar relation, replacing x_i^{lq} —the mole fraction of the i-th component in the liquid phase—with an effective quantity—the activity a_i, and $r_i'(T)$ with a function of the temperature and pressure—$\varphi_i(T, p)$:

$$\mu_i^{lq} = RT \ln a_i + \varphi_i(T, p) \tag{2.12}$$

The activity a_i replaces the mole fraction and characterizes the composition of a mixture. Naturally, for an individual substance $a_i = x_i^{lq} = 1$. Hence, for an individual substance i, we have

$$\mu_i^\circ = RT \ln f_i^\circ + r_i(T), \quad \mu_i^{lq\circ} = \varphi_i(T, p)$$

Since $\mu_i^\circ = \mu_i^{lq\circ}$, then

$$\varphi_i(T, p) = RT \ln f_i^\circ + r_i(T), \quad \mu_i^{lq} = RT \ln a_i f_i^\circ + r_i(T) \tag{2.13}$$

Equating the right-hand sides of Eqs. (2.11) and (2.13), we obtain an equation for calculating the activity:

$$a_i = \frac{f_i}{f_i^\circ} \tag{2.14}$$

In a particular case when the vapour in equilibrium with a solution can be considered to be an ideal gas mixture, we have $f_i = p_i$, $f_i^\circ = p_i^\circ$, and

$$a_i = \frac{p_i}{p_i^\circ} \tag{2.15}$$

Thus, the introduction of the activity a_i allows us to obtain an expression for the chemical potential of a real solution, while the value of the activity a_i can be determined, for example, from the fugacities (pressures) of the saturated vapour pressure of a component over the solution (f_i, p_i) and over the relevant individual component (f_i°, p_i°).

From the condition that $\Delta(\nu_i \mu_i) = 0$ for reactions in a real solution that holds for any systems, we have:

$$\Delta(\nu_i \mu_i^{lq}) = \Delta\{\nu_i [RT \ln a_i + \varphi_i(T, p)]\} = 0$$

Therefore, equilibrium in a real solution can be characterized by the constant K_a; here

$$K_a = \prod_{i'} a_i'^{\nu_i'} \Big/ \prod_i a_i^{\nu_i} = \exp\left[-\frac{\Delta\nu_i \varphi_i(T, p)}{RT}\right],$$

$$K_a = K_a(T, p)$$

Since by Eq. (2.14) $a_i = f_i/f_i^\circ$, we can obtain

$$K_a = (\prod_{i'} f_i'^{\nu_i'}/\prod_i f_i^{\nu_i})/(\prod_{i'} f_i^{\circ\nu_i'}/\prod_i f_i^{\circ\nu_i}) = K_f K_{f^\circ} \qquad (2.16)$$

The constant K_f characterizes chemical equilibrium in a real gas mixture in equilibrium with a real liquid. How this constant is calculated was treated in Sec. 2.3. The quantity K_{f° is determined from the fugacities of the individual substances at the temperature of the reaction and the pressure of their saturated vapour. The above expressions establish the possibility in principle of calculating equilibrium in a real solution.

2.6. Heterogeneous Reactions

Heterogeneous reactions conducted in systems with the reactants in two (gas-liquid, liquid-solid, gas-solid) or three (gas-liquid-solid) phases include the hydrogenation of coal, coal pastes, and petroleum residues, the preparation of acetylene from calcium carbide [$CaC_2(s) + H_2O(lq) \rightarrow CaO(s) + C_2H_2(g)$], and many other transformations.

Assume that the following reaction proceeds:

$$\nu_1A_1 + \nu_2A_2 + \ldots + \rho_1B_1 + \rho_2B_2 + \ldots \rightarrow \nu_1'A_1' + \nu_2'A_2' + \ldots + \rho_1'B_1' + \rho_2'B_2' + \ldots$$

where $A_1, A_2, \ldots, A_1', A_2', \ldots$ are gaseous reactants and products with the relevant stoichiometric coefficients ν, and $B_1, B_2, \ldots, \ldots, B_1', B_2', \ldots$ are liquid or solid reactants and products with the relevant stoichiometric coefficients ρ.

It must be stressed that for all the components of a reacting mixture (gaseous, liquid, and solid), one can determine the standard thermodynamic functions and from them—the standard heat of a reaction ΔH°, entropy increment ΔS°, and change in the Gibbs energies ΔG° for a heterogeneous reaction. The required quantities are generally given in standard thermodynamic tables. The task arises, however, of using the value of ΔG° for calculating equilibrium compositions.

The condition $\Delta G = \Delta(\nu_i\mu_i)$ holds for reactions in any systems because it has been obtained without any assumptions on the phase state of the reactants.

For gaseous substances, their chemical potentials $\mu_{i,g}$ are expressed in terms of the fugacity f_i:

$$\mu_{i,g} = RT \ln f_i + r_i(T)$$

For substances in a condensed phase (liquid or solid solutions), their chemical potentials $\mu_{i\,cond}$ can be expressed in terms of the

activity a_i:

$$\mu_{i,\text{cond}} = RT \ln a_i + \varphi_i(T)$$

where r_i and φ_i are arbitrary functions of the temperature.

In the equilibrium of isobaric-isothermal or isochoric-isothermal reactions, as has been shown above, the general condition of equilibrium of both homogeneous and heterogeneous reactions has the form

$$\Delta G = \Delta(\nu_i \mu_i) = 0$$

or

$$\Delta(\nu_{i,g}\mu_{i,g}) + \Delta(\rho_{i,\text{cond}}\mu_{i,\text{cond}}) = 0 \tag{2.17}$$

where the first term on the left-hand side determines the change in the products $(\nu_i \mu_i)$ for gaseous, and the second one—for condensed reactants.

Introducing into this condition the expressions for $\mu_{i,g}$ and $\mu_{i,\text{cond}}$, we find:

$$\Delta(\nu_{i,g}\mu_{i,g}) = RT \ln \frac{f_{A_1'}^{\nu_1'} f_{A_2'}^{\nu_2'} \cdots}{f_{A_1}^{\nu_1} f_{A_2}^{\nu_2} \cdots} + \Delta(\nu_i r_i) \tag{2.18}$$

$$\Delta(\rho_{i,\text{cond}}\mu_{i,\text{cond}}) = RT \ln \frac{a_{B_1'}^{\rho_1'} a_{B_2'}^{\rho_2'} \cdots}{a_{B_1}^{\rho_1} a_{B_2}^{\rho_2} \cdots} + \Delta(\rho_i \varphi_i) \tag{2.19}$$

Inserting Eqs. (2.18) and (2.19) into (2.17), we obtain:

$$\ln \left[\frac{f_{A_1'}^{\nu_1'} f_{A_2'}^{\nu_2'} \cdots}{f_{A_1}^{\nu_1} f_{A_2}^{\nu_2} \cdots} \frac{a_{B_1'}^{\rho_1'} a_{B_2'}^{\rho_2'} \cdots}{a_{B_1}^{\rho_1} a_{B_2}^{\rho_2}} \right] = -\frac{\Delta(\nu_i r_i) + \Delta(\rho_i \varphi_i)}{RT} = g(T, p)$$

Consequently, for a heterogeneous reaction, the equilibrium constant is

$$K_{f,a} = \frac{f_{A_1'}^{\nu_1'} f_{A_2'}^{\nu_2'} \cdots}{f_{A_1}^{\nu_1} f_{A_2}^{\nu_2} \cdots} \cdot \frac{a_{B_1'}^{\rho_1'} a_{B_2'}^{\rho_2'} \cdots}{a_{B_1}^{\rho_1} a_{B_2}^{\rho_2}} \tag{2.20}$$

If stoichiometric amounts react ($\Delta\lambda = 1$), and the fugacities and activities of the reactants in the initial mixture ($f_{i,0}$ and $a_{i,0}$) differ from their equilibrium values, then at p, T = const:

$$\Delta G = \Delta(\nu_i \mu_i) = RT \left[\ln \frac{f_{0,A_1'}^{\nu_1'} f_{0,A_2'}^{\nu_2'} \cdots a_{0,B_1'}^{\rho_1'} \cdots}{f_{0,A_1}^{\nu_1} f_{0,A_2}^{\nu_2} \cdots a_{0,B_1}^{\rho_1}} - \ln K_{f,a} \right] \tag{2.21}$$

Equation (2.21) is an equation of a heterogeneous reaction isotherm. Thus, for a heterogeneous reaction, thermodynamics validates expressions of the law of mass action (2.20) and an isotherm (2.21) similar to those for homogeneous gas reactions.

If $\Delta G < 0$, the equilibrium values of the quantities f_i and a_i in the expression for $K_{f,a}$ are smaller than the initial ones ($f_{i,0}$ and $a_{i,0}$), and the reaction will proceed from the left to the right. At $\Delta G = 0$, the system is in equilibrium. If, on the other hand, $\Delta G > 0$, the reverse reaction may proceed.

If we consider that the state is standard for gaseous reactants when $f_{0,A_1} = f_{0,A_2} = \ldots = f_{0,A_1'} = f_{0,A_2'} = \ldots = f^\circ$, and for condensed ones when $a_{0,B_1} = a_{0,B_2} = \ldots = a_{0,B_1'} = a_{0,B_2'} = \ldots = 1$, then

$$\Delta G^\circ = -RT \ln K^\circ_{f,a} = \Delta H^\circ - T\Delta S^\circ$$

But although the determination of the quantity ΔG° involves no fundamental difficulties, the use of this quantity for calculating the composition of an equilibrium mixture in a non-ideal system is very complicated owing to difficulties in determining the quantities a_i and f_i. In essence, the relations treated above, if no simplifications are employed, only indicate the possibility of performing calculations. The actual performance of the calculations for each specific heterogeneous reaction, however, becomes an independent problem.

The calculations by Eqs. (2.21) are simplified if the gas and condensed phases can be considered ideal. In this case, $f_i = p_i$ and $a_i = x_i$ (where p_i and x_i are the partial pressure of the gaseous component and the mole fraction of the condensed one), and therefore

$$K_{f,a} = K_{p,x} = \frac{p_{A_1}^{\nu_1'} p_{A_2}^{\nu_2'} \ldots}{p_{A_1}^{\nu_1} p_{A_2}^{\nu_2} \ldots} \frac{x_{B_1}^{\rho_1'} x_{B_2}^{\rho_2'} \ldots}{x_{B_1}^{\rho_1} x_{B_2}^{\rho_2} \ldots} \tag{2.22}$$

If only one substance is present in the liquid or solid phase, its activity (concentration) does not change in the course of the reaction and depends only on the temperature. If the solid phase contains several substances, but they are sparingly soluble in one another, their activities do not change in the course of the reaction and depend only on the temperature.

Heterogeneous Reactions in a System Including an Ideal Gas, an Ideal Liquid Solution, and a Mixture of Solids. We shall write the reaction equation in the form:

$$\sum \nu_i A_i + \sum \rho_i B_i + \sum \delta_i C_i \rightarrow \sum \nu_i' A_i' + \sum \rho_i' B_i' + \sum \delta_i' C_i'$$

where ν, ρ, and δ are stoichiometric coefficients, A are gaseous, B—liquid, and C—solid reactants; the quantities relating to the products are primed. The quantity ΔG for this reaction is related to the chemical potentials of the components by the usual equation:

$$\Delta G = \Delta(\nu_i \mu_{i,g}) + \Delta(\rho_i \mu_{i,lq}) + \Delta(\delta_i \mu_{i,s})$$

where $\mu_{i,g}$, $\mu_{i,lq}$, and $\mu_{i,s}$ are the chemical potentials of a gaseous, liquid, and solid reactants, respectively. They can be expressed as

follows:

$$\mu_{i,g} = RT \ln p_i + r_i(T), \quad \mu_{i,lq} = RT \ln x_i + \varphi_i(T), \quad \mu_{i,s} = d_i(T)$$

It has been assumed here that the composition of a solid does not change ($x_{i,s} = 1$, there are no solid solutions), and its chemical potential is independent of the pressure (this holds for not very high pressures).

Now, if a reaction is conducted with a mixture in which the initial partial pressures are $p_{0,i}$ and the mole fractions are $x_{0,i}$, then at T,p = const:

$$\Delta G = RT \ln \left[\frac{p_{0,A_1}^{\nu_1'} p_{0,A_2}^{\nu_2'} \cdots}{p_{0,A_1}^{\nu_1} p_{0,A_2}^{\nu_2} \cdots} \cdot \frac{x_{0,B_1}^{\rho_1'} x_{0,B_2}^{\rho_2'} \cdots}{x_{0,B_1}^{\rho_1} x_{0,B_2}^{\rho_2} \cdots} \right] + \Delta(\nu_i r_i) + (\rho_i \varphi_i) + \Delta(\delta_i d_i)$$

In equilibrium, $p_{0,i} = p_i$, $x_{0,i} = x_i$, $\Delta G = 0$, and

$$\ln K_{p,x} = -\frac{\Delta(\nu_i r_i) + \Delta(\rho_i \varphi_i) + \Delta(\delta_i d_i)}{RT}$$

The equation of an isotherm therefore becomes

$$\Delta G = RT \left[\ln \frac{p_{0,A_1}^{\nu_1'} p_{0,A_2}^{\nu_2'} \cdots}{p_{0,A_1}^{\nu_1} p_{0,A_2}^{\nu_2} \cdots} \cdot \frac{x_{0,B_1}^{\rho_1'} x_{0,B_2}^{\rho_2'} \cdots}{x_{0,B_1}^{\rho_1} x_{0,B_2}^{\rho_2}} - \ln K_{p,x} \right] \quad (2.23)$$

If we consider that the state is standard for gases when $p_{0,i} = p^\circ$ and for liquids when $x_{0,i} = 1$, then the standard change in the Gibbs energy is

$$\Delta G^\circ = RT \ln K_{p,x}^\circ$$

where $K_{p,x}^0 = K_{p,x}/(p^\circ)^{\sum \nu_i}$ and $\sum \nu_i \equiv \Delta\nu_i$. The latter condition enables one to calculate the equilibrium of heterogeneous reactions.

For example, for the reaction

$$CaC_2(s) + 2H_2O(lq) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$$

using standard thermodynamic tables, we find

$$\Delta G^\circ = -\{\Delta G_f^\circ(CaC_2) + 2\Delta G_f^\circ(H_2O) + [\Delta G_f^\circ(Ca(OH)_2) + \Delta G_f^\circ(C_2H_2)]\}$$

Since

$$K_{p,x} = \frac{p(C_2H_2)\, x\, [Ca(OH)_2]_s}{x(CaC_2)_s\, x^2(H_2O)_{lq}}$$

we have

$$\Delta G^\circ = -RT \ln \left\{ \frac{p(C_2H_2)\, x\, [Ca(OH)_2]_s}{x^2(H_2O)_{lq}\, x(CaC_2)_s} (p^\circ)^{-1} \right\}$$

By expressing p_i and x_i in terms of one variable (the degree of conversion), we can find the composition of the equilibrium mixture.

Similarly for the reaction $C + CO_2 \rightarrow 2CO$, we have:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln \left[\frac{p^2(CO)}{p(CO_2)} \frac{1}{p^\circ} \right]$$

For this reaction,

$$\Delta H^\circ_{298} = [-110.54 \times 2 - (-393.50 + 0)] = 172.42 \text{ kJ}$$
$$\Delta S^\circ_{298} = [198.11 \times 2 - (213.93 \times 5.75)] = 176.54 \text{ J/K}$$
$$\Delta G^\circ_{298} = 172.42 - 298 \times 176.54 \times 10^{-3} = 119.81 \text{ kJ}$$

This signifies that at 298 K the reaction being considered should not be conducted because its equilibrium constant is negligibly small. Elevation of the temperature is attended by a decrease in ΔG° and an increase in the thermodynamic probability and equilibrium constant of the reaction.

For the reaction

$$CaC_2(s) + 2H_2O(lq) \rightarrow Ca(OH)_2(s) + C_2H_2$$
$$\Delta H^\circ_{298} = (-986.20 + 226.75) - [-62.70 + 2(-285.84)] = -125 \text{ kJ}$$
$$\Delta S^\circ_{298} = (83.4 + 200.8) - (70.3 + 2 \times 70.0) = 74 \text{ J/K}$$
$$\Delta G^\circ_{298} = -125 - 298 \times 74 \times 10^{-3} = 147 \text{ kJ}$$

For 298 K, the equilibrium constant is

$$K^\circ_p = \exp\left(\frac{147}{8.31 \times 298 \times 10^{-3}}\right) = \exp(59.4)$$
$$K_{p,x} = K^\circ_p p^\circ = 0.1 \exp(59.4) \text{ MPa}$$

If the water, calcium carbide, and calcium hydroxide form independent phases, then $x(CaC_2)_s = x(H_2O)_{lq} = x[Ca(OH)_2]_s = 1$, and $K_{p,x} = p(C_2H_2)$. At the calculated value of $K_{p,x}$, the reaction will proceed virtually to the end.

The above two particular examples are encountered in practical calculations the most frequently, namely, a heterogeneous reaction proceeds to the end or, conversely, it involves a negligible amount of the feed stock. Situations are encountered, however, when reactions in the gas phase are thermodynamically unfavourable, but the transition to a heterogeneous (gas-liquid) reaction enables one to lower the thermodynamic restrictions as, for example, for some reactions of CO and CO_2 (see Chap. 8).

Let us now consider an important particular case of heterogeneous reactions.

Heterogeneous Reactions in a Gas-Liquid System. In many reactions (chemisorption, alkylation, cracking, hydrogenation, oxidation, etc.), a part of the reactants are in the gas and a part in the liquid phase. The equation of the reaction can be written as

$$\sum \nu_i A_i + \sum \rho_k B_k \rightarrow \sum \nu'_i A'_i + \sum \rho'_k B'_k$$

where ν_i and A_i are the stoichiometric coefficient and symbol of a gaseous reactant, respectively, ρ_k and B_k are the same for a liquid reactant; the primed quantities relate to the products. The calculations for such reactions are performed on the basis of the data of standard

thermodynamic tables. The values of the quantities $C^{\circ}_{p,i}$, S°_{i}, $\Delta H^{\circ}_{f,i}$, and $\log K_{p,f,i}$ can be given either only for the gas state of all the components, or both for the gas and liquid ones.

Thermodynamic calculations are the simplest if we assume that the liquid phase is an ideal solution and the gas phase is an ideal gas. This case is just what we shall consider below.

Generally, the product of a heterogeneous reaction can also be obtained by reacting the substances only in the gas phase. For example, alkylation using gaseous propylene can be performed with benzene both in the liquid and the gas phases. It is therefore useful to compare the thermodynamic characteristics of processes occurring in a gas-liquid (glq) system or only in a gas (no index) one.

A. The heats of a reaction ΔH^{glq} in a gas-liquid phase and ΔH in only a gas one are related to the heats of vaporization ΔH^{v} and condensation ΔH^{cond} of the reactants:

$$\Delta H^{\text{glq}} = \Delta H + \left(\sum \rho_k \Delta H^{\text{v}}_{\text{B}_k} - \sum \rho'_k \Delta H^{\text{cond}}_{\text{B}'_k}\right) \tag{2.24}$$

The expression in parentheses in Eq. (2.24) is usually small, and the heats ΔH^{glq} and ΔH are close in value.

B. The heats of a reaction ΔH^{glq} at constant pressure and ΔU^{glq} at constant volume are related by the usual expression

$$\Delta H^{\text{glq}} = \Delta U^{\text{glq}} + p\Delta v$$

Since the volume of the liquid phase does not change appreciably, ΔU characterizes the change in the volume at the expense of the reaction of only the gaseous components. Consequently, at $T, p =$ $=$ const, we have:

$$\Delta H^{\text{glq}} = \Delta U^{\text{glq}} + \left(\sum \nu'_i - \sum \nu_i\right) RT \tag{2.25}$$

C. The temperature dependence of the heat of a reaction is determined by Kirchhoff's equation, so that

$$\Delta H^{\text{glq}}_{T} = \Delta H^{\text{glq}}_{T_0} + \int_{T_0}^{T} \left[\left(\sum \nu_{i'} C_{p,\text{A}'_i} + \sum \rho_{k'} C_{p,\text{B}'_k}\right) - \left(\sum \nu_i C_{p,\text{A}_i} + \sum \rho_k C_{p,\text{B}_k}\right)\right] dT \tag{2.26}$$

For an ideal system, ΔH^{glq} and ΔU^{glq} do not depend on the pressure.

For gaseous components

$$\mu_i = RT \ln p_i + r_i(T)$$

For liquid-phase components with account taken of Raoult's law

$$\mu_i = RT \ln x_i + \varphi_i(T)$$

Introducing the expressions for the chemical potentials into the equation for ΔG^{glq} for an equilibrium system ($\Delta G^{glq} = 0$, p_i and x_i are the equilibrium partial pressures of the gaseous components and the mole fractions of the liquid components, respectively), we find

$$\Delta G^{glq} = 0 = RT \ln \left[\left(\frac{p_{A_1}^{\nu_1'} p_{A_2}^{\nu_2'} \cdots}{p_{A_1}^{\nu_1} p_{A_2}^{\nu_2} \cdots} \right) \left(\frac{x_{B_1}^{\rho_1'} x_{B_2}^{\rho_2'} \cdots}{x_{B_1}^{\rho_1} x_{B_2}^{\rho_2} \cdots} \right) \right] + \Delta (\nu_i r_i) + \Delta (\rho_i \varphi_i) \tag{2.27}$$

Let us denote the fractions in parentheses by K_p and K_x, and their product by $K_{p,x}$. Hence

$$\ln K_{p,x} = -\frac{\Delta (\nu_i r_i) + \Delta (\rho_i \varphi_i)}{RT} = \ln (K_p)(K_x) = \ln \left[\left(\prod p_{A_i}^{\nu_i} \right) \left(\prod x_{B_i}^{\rho_i} \right) \right] \tag{2.28}$$

Thus, the equilibrium constant of a gas-liquid reaction is the product of two partial constants, namely, K_p only for the gaseous components and K_x only for the liquid-phase ones.

For example, for the reaction of alkylation of liquid benzene with gaseous propylene with the formation of a liquid alkylbenzene, we have:

$$K_p = \frac{1}{p\,(C_3H_6)}, \quad K_x = \frac{x\,(C_6H_5C_3H_7)}{x\,(C_6H_6)}, \quad K_{p,x} = \frac{x\,(C_6H_5C_3H_7)}{p\,(C_3H_6)\,x\,(C_6H_6)}$$

If a reaction is conducted in a system where the initial partial pressures $p_{i,0}$ of the gaseous components and the mole fractions $x_{i,0}$ of the liquid ones differ from their equilibrium values, then by inserting the expressions for the chemical potentials into the equation $\Delta G^{glq} = \Delta (\nu_i \mu_{i,0})$ and taking into account condition (2.28), we obtain the equation of an isotherm:

$$\Delta G^{glq} = RT \left[\ln \frac{p_{0,A_1'}^{\nu_1'} p_{0,A_2'}^{\nu_2'} \cdots}{p_{0,A_1}^{\nu_1} p_{0,A_2}^{\nu_2} \cdots} \cdot \frac{x_{0,B_1'}^{\rho_1'} x_{0,B_2'}^{\rho_2'} \cdots}{x_{0,B_1}^{\rho_1} x_{0,B_2}^{\rho_2} \cdots} - \ln K_{p,x} \right] \tag{2.29}$$

For the usual standard states of a gas and liquid ($p_{i,0} = p^\circ$ and $x_{i,0} = 1$), we have:

$$\Delta G^\circ = -RT \ln K_{p,x}^\circ \tag{2.30}$$

Since we can find the value of ΔG° from the data of standard thermodynamic tables, i.e. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, while ΔH° and ΔS° are determined from the heats of formation and the absolute entropies of substances, there are no difficulties in determining $K^\circ_{p,x}$ with the aid of Eq. (2.30).

It must be stressed that if in the initial (prior to a reaction) and final (equilibrium after the reaction) systems phase equilibrium sets

in, then owing to the equality of the chemical potentials of each component in both phases, the values of ΔG for the gaseous and gas-liquid reactions are the same.

D. If both the gas and liquid phases are not ideal, the fugacities f_i should be substituted for the partial pressures p_i and the activities a_i for the mole fractions x_i in the solution in the expressions for $K_{p,x}$. Therefore, for non-ideal gas and liquid phases, we have

$$K_{f,a} = \frac{f_{A_1'}^{\nu_1'} f_{A_2'}^{\nu_2'} \cdots}{f_{A_1}^{\nu_1} f_{A_2}^{\nu_2} \cdots} \cdot \frac{a_{B_1'}^{\rho_1'} a_{B_2'}^{\rho_2'} \cdots}{a_{B_1}^{\rho_1} a_{B_2}^{\rho_2} \cdots} \tag{2.31}$$

$$\Delta G^{\mathrm{glq}} = RT \left\{ \ln \frac{f_{0,A_1'}^{\nu_1'} f_{0,A_2'}^{\nu_2'} \cdots}{f_{0,A_1}^{\nu_1} f_{0,A_2}^{\nu_2} \cdots} \cdot \frac{a_{0,B_1'}^{\rho_1'} a_{0,B_2'}^{\rho_2'} \cdots}{a_{0,B_1}^{\rho_1} a_{0,B_2}^{\rho_2} \cdots} - \ln K_{f,a} \right\} \tag{2.32}$$

The difficulties involved in determining the activities for real solutions of organic substances have been noted above. Therefore, the cited general relations illustrate only a possible approach. In each specific case of a gas-liquid reaction in non-ideal systems, thermodynamic calculations pose a number of unique problems.

E. When calculating the equilibrium degree of conversion y from the value of the constant $K_{p,x}$, one should use the expression in terms of the conversion of the instantaneous masses of the components. Let us illustrate the calculations of the equilibrium degree of conversion for the sufficiently general reaction

$$\nu A + \rho B = \nu' A' + \rho' B'$$

Two cases are possible.

1. The reaction is conducted at constant temperature and pressure in a gas-liquid stream, the following amounts of the components (in mol/s) being introduced into the reactor: $m_{0,B} = m_0$, $m_{0,A} = \delta_A m_0$, $m_{0,B'} = \delta_{B'} m_0$, $m_{0,A'} = \delta_{A'} m_0$. It is convenient to express the degree of conversion relative to the liquid reactant B so that $m_B = m_0(1 - y)$. The equilibrium amounts of the other reactants are as follows:

$$m_A = m_0 \left(\delta_A - \frac{\nu}{\rho} y \right), \quad m_{A'} = m_0 \left(\delta_{A'} + \frac{\nu'}{\rho} y \right),$$

$$m_{B'} = m_0 \left(\delta_{B'} + \frac{\rho'}{\rho} y \right)$$

The sum of the moles of the gas-phase components is

$$\sum m_i = m_A + m_{A'} = m_0 \left(\delta_A + \delta_{A'} + \frac{\nu' - \nu}{\rho} y \right)$$

and of the liquid-phase ones is

$$\sum m_i (\mathrm{lq}) = m_B + m_{B'} = m_0 \left[1 + \delta_B + \left(\frac{\rho'}{\rho} - 1 \right) y \right]$$

The mole fractions of the components in the gas phase are

$$x_A = \frac{\delta_A - (\nu/\rho)\, y}{\delta_A + \delta_{A'} + [(\nu' - \nu)/\rho]\, y}, \quad x_{A'} = \frac{\delta_{A'} + (\nu'/\rho)\, y}{\delta_A + \delta_{A'} + [(\nu' - \nu)/\rho]\, y}$$

and those of the components in the liquid phase are

$$x_B = \frac{1 - y}{1 + \delta_{B'} + [(\rho'/\rho) - 1]\, y}, \quad x_{B'} = \frac{\delta_{B'} + (\rho'/\rho)\, y}{1 + \delta_{B'} + [(\rho'/\rho) - 1]\, y}$$

It is now a simple matter to express $K_{p,x}$ as a function of y:

$$K_{p,x} = \frac{x_{B'}^{\rho'}}{x_B^{\rho_B}} \cdot \frac{p_{A'}^{\nu'}}{p_A^{\nu_A}} = \frac{[\delta_{B'} + (\rho'/\rho)\, y]^{\rho'}}{(1-y)^{\rho}\left[1 + \delta_{B'} + \left(\frac{\rho'}{\rho} - 1\right) y\right]^{\rho' - \rho}}$$

$$\times \frac{[\delta_{A'} + (\nu'/\rho)\, y]^{\nu'}}{\left(\delta_A - \frac{\nu}{\rho}\, y\right)^{\nu}\left[\delta_A + \delta_{A'} + \frac{\nu' - \nu}{\rho}\, y\right]^{\nu' - \nu}}\, p^{\nu' - \nu}$$

In the particular case when $\nu' = \nu = \rho' = \rho = 1$ and $\delta_{A'} = \delta_{B'} = 0$, we have

$$K_{p,x} = \frac{y^2}{(1-y)(\delta_A - y)}$$

2. A reaction is conducted at constant temperature and pressure by bubbling gaseous reactant A through a liquid containing liquid reactant B and product B′. The conditions of conducting the reaction themselves favour the complete using up of reactant B (the degree of conversion is close to unity). Indeed, with intensive bubbling, the total pressure in the system is produced by reactant A, namely, $p \approx p_A$, and the partial pressure of product A′ is close to zero: $p_{A'} \approx 0$. Since

$$K_{p,x} = \frac{x_{B'}^{\rho'} p_{A'}^{\nu'}}{x_B^{\rho} p_A^{\nu}}$$

then when the value of $K_{p,x}$ is limited and $p_{A'} \approx 0$, it is necessary that $x_B \approx 0$. This signifies that reactant B is practically absent in the equilibrium mixture. Naturally, everything said above holds if $K_{p,x}$ is noticeably larger than zero. At negligibly small values of $K_{p,x}$ (the reaction has a low probability thermodynamically), the condition $p_{A'} = 0$ (no product forms) leads to $K_{p,x} = 0$ even when $x_B = 1$ (the reactant is not consumed).

Chapter 3

Calculation of the Equilibrium Composition of Complex Reactions

In the preceding chapter, we have treated thermodynamic analysis for cases when chemical changes are described by one stoichiometric equation and one equilibrium constant—this is what we call a simple reaction. In the overwhelming majority of real processes, there simultaneously proceed several reactions or, as we say, a complex reaction. Such processes are characterized by several stoichiometric equations and accordingly by several equilibrium constants. This is why below we consider the determination of the equilibrium composition for a mixture of substances participating in a number of reactions. We shall call this case **complex equilibrium**.

In complex equilibrium, the heats and equilibrium constants for each simple step (simple reaction) are determined in the same way as if only this reaction proceeded in the system. The procedures for such calculations are described in Chap. 2. A new problem arises, however, namely, the calculation of the equilibrium concentrations satisfying all the equilibrium constants of the simple reactions.

If a complex reaction consisting of p simple ones and characterized by the same number of equilibrium constants K_x proceeds in a system, while the number of reactants is n, we have to use p equations of the law of mass action to find n unknown equilibrium concentrations, for example, from the system:

$$\left.\begin{aligned} K_{x_1} &= \prod_i{}_1 x_i^{\nu_i} \\ K_{x_2} &= \prod_i{}_2 x_i^{\nu_i} \\ K_{x_p} &= \prod_i{}_p x_i^{\nu_i} \end{aligned}\right\} \quad i = 1, 2, \ldots, n \tag{3.1}$$

If one of the equations is not independent, for example if the last one can be obtained as the product of the first two: $K_{x_p} = K_{x_1}K_{x_2}$ and $\prod_i{}_p = \prod_i{}_1 \prod_i{}_2$, it is superfluous and carries no information. Consequently, in a system of equations relating known equilibrium constants and unknown concentrations, all the equilibrium constants and all the reactions must be independent so that none of them could be

obtained by combining the others. Let us therefore consider the procedure for choosing a p_1 independent reaction from among p reactions proceeding in a system.

3.1. Independent Reactions

Assume that we have a system of p linear equations:

$$\sum_{i=1}^{n} \nu_{ij} z_i = 0, \quad j = 1, 2, \ldots, p$$

where ν_{ij} are constant coefficients and z_i are variables. It is shown in linear algebra that these equations will be linearly independent, i.e. none of them can be obtained by combining the remaining ones if the rank of the matrix of the constant coefficients

$$\underline{\nu} = \begin{vmatrix} \nu_{11} & \nu_{21} & \ldots & \nu_{n1} \\ \nu_{12} & \nu_{22} & \ldots & \nu_{n2} \\ \nu_{1p} & \nu_{2p} & \ldots & \nu_{np} \end{vmatrix}$$

equals p. To determine the rank of a matrix, it is transformed so that part of the rows consist of zeros. The number of remaining rows where not all the elements are equal to zero equals the rank of the matrix. Here the following transformations of the matrix rows can be used: multiplication (or division) by a constant coefficient, addition (or subtraction) with another row. Therefore, the transformation of a matrix of coefficients for determining its rank can be performed by employing the following alternating procedures [10, 13].

We initially divide the first row by ν_{11} ($\nu_{11} \neq 1$) so that the first element of this row becomes equal to unity. Next we subtract from each following row f the first one multiplied by ν_{1f} and obtain a matrix with zeros in the first column:

$$\begin{vmatrix} \nu_{11} & \nu_{21} & \ldots & \nu_{n1} \\ \nu_{12} & \nu_{22} & \ldots & \nu_{n2} \\ \nu_{1p} & \nu_{2p} & \ldots & \nu_{np} \end{vmatrix} \xrightarrow{(a)} \begin{vmatrix} 1 & \frac{\nu_{21}}{\nu_{11}} & \ldots & \frac{\nu_{n1}}{\nu_{11}} \\ \nu_{12} & \nu_{22} & \ldots & \nu_{n2} \\ \nu_{1p} & \nu_{2p} & \ldots & \nu_{np} \end{vmatrix} \xrightarrow{(b)}$$

$$\rightarrow \begin{vmatrix} 1 & \frac{\nu_{21}}{\nu_{11}} & \ldots & \frac{\nu_{n1}}{\nu_{11}} \\ 0 & \nu_{22} - \nu_{12}\frac{\nu_{21}}{\nu_{11}} & \ldots & \nu_{n2} - \nu_{12}\frac{\nu_{n1}}{\nu_{11}} \\ \cdot & \cdot & \cdot & \cdot \\ 0 & \nu_{2p} - \nu_{1p}\frac{\nu_{21}}{\nu_{11}} & \ldots & \nu_{np} - \nu_{1p}\frac{\nu_{n1}}{\nu_{11}} \end{vmatrix}$$

After this, we repeat operations (a) and (b) to transform the second diagonal element of the matrix to unity and obtain zeros in the second column:

$$\begin{vmatrix} 1 & \frac{\nu_{21}}{\nu_{11}} & \dots & \frac{\nu_{n1}}{\nu_{11}} \\ 0 & \nu_{22}-\nu_{12}\frac{\nu_{21}}{\nu_{11}} & \dots & \nu_{n2}-\nu_{12}\frac{\nu_{n1}}{\nu_{11}} \\ \dots & \dots & \dots & \dots \\ 0 & \nu_{2p}-\nu_{1p}\frac{\nu_{21}}{\nu_{11}} & \dots & \nu_{np}-\nu_{1p}\frac{\nu_{n1}}{\nu_{11}} \end{vmatrix} \xrightarrow{(a)}$$

$$\rightarrow \begin{vmatrix} 1 & \frac{\nu_{21}}{\nu_{11}} & \dots & \frac{\nu_{n1}}{\nu_{11}} \\ 0 & 1 & \dots & \dfrac{\nu_{n2}-\nu_{12}\frac{\nu_{n1}}{\nu_{11}}}{\nu_{22}-\nu_{12}\frac{\nu_{21}}{\nu_{11}}} \\ \dots & \dots & \dots & \dots \\ 0 & \nu_{2p}-\nu_{1p}\frac{\nu_{21}}{\nu_{11}} & \dots & \nu_{np}-\nu_{1p}\frac{\nu_{n1}}{\nu_{11}} \end{vmatrix} \xrightarrow{(b)}$$

$$\rightarrow \begin{vmatrix} 1 & \frac{\nu_{21}}{\nu_{11}} & \dots & \frac{\nu_{n1}}{\nu_{11}} \\ 0 & 1 & \dots & \dfrac{\nu_{n2}-\nu_{12}\frac{\nu_{n1}}{\nu_{11}}}{\nu_{22}-\nu_{12}\frac{\nu_{21}}{\nu_{11}}} \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \nu_{np}-\nu_{1p}\frac{\nu_{n1}}{\nu_{11}}-\left(\nu_{2p}-\nu_{1p}\frac{\nu_{2p}}{\nu_{11}}\right)\dfrac{\nu_{n2}-\nu_{12}\frac{\nu_{n1}}{\nu_{11}}}{\nu_{22}-\nu_{12}\frac{\nu_{21}}{\nu_{11}}} \end{vmatrix}$$

Operations (a) and (b) are further repeated consecutively for each row after the second one. If after completing operations (a) and (b) for all the rows we do not obtain a single row all of whose elements equal zero, this signifies that all the reactions are independent. If among the p rows of the matrix we obtained g rows all of whose elements became equal to zero, the rank of the matrix and the number of independent equations equal $p - g$.

The same approach is convenient for determining the number of independent reactions. Here it is convenient to represent the stoichiometric equations in the form of conventional algebraic ones:

$$\sum_i \nu_{ij} A_i = 0$$

In this form of equation, the stoichiometric coefficients of the reactants are negative, and of the products, positive. For example, we write the stoichiometric equation of the reaction of dehydrogenation of cyclohexane in the form

$$-C_6H_{12}+C_6H_6+3H_2=0$$

It must be stressed that the general condition for the independence of simple reactions, like the condition of the independence of linear equations, can be stated as follows: if with any choice of the constant quantity f_i we cannot obtain $\sum_i f_i\nu_{ij} = 0$ (f_i must not equal zero), the equations are independent. It is exactly this general condition that results in the rank of a matrix of independent equations being equal to the number of these equations.

The considered procedure for determining the number of independent equations utilizes the circumstance that the equations of chemical reactions

$$-\nu_{11}A_1-\nu_{12}A_2-\ldots+\nu'_{11}A'_1+\nu'_{12}A'_2+\ldots=0$$
$$-\nu_{21}A_1-\nu_{22}A_2-\ldots+\nu'_{21}A'_1+\nu'_{22}A'_2+\ldots=0$$

can be written in the form

$$-A_1-\frac{\nu_{12}}{\nu_{11}}A_2-\ldots+\frac{\nu'_{11}}{\nu_{21}}A'_1+\frac{\nu'_{22}}{\nu_{11}}A'_2+\ldots=0$$
$$-A_1-\frac{\nu_{22}}{\nu_{21}}A_2-\ldots+\frac{\nu'_{21}}{\nu_{21}}A'_1+\frac{\nu'_{21}}{\nu_{21}}A'_2+\ldots=0$$

Further, subtracting the first equation from the second one, we obtain a dependent stoichiometric equation in which A_1 is absent. The equilibrium constant of this new equation equals the ratio of the equilibrium constants of the reactions by combining which it has been obtained. Hence, if similar operations enable us to obtain a dependent reaction in which all the stoichiometric coefficients are zero, there are dependent reactions among the initial ones.

Let us first illustrate the determination of the number of independent equations for a comparatively simple case—the hydroisomerization of benzene. The equations of the simple steps (the hydrogenation of benzene to cyclohexane, the hydroisomerization of benzene to methylcyclopentane, and the isomerization of cyclohexane to methylcyclopentane) are as follows:

$$-C_6H_6-3H_2+C_6H_{12}=0 \qquad -1A_1-3A_2+1A_3+0A_4=0$$
$$-C_6H_6-3H_2+C_5H_9CH_3=0 \quad \text{or} \quad -1A_1-3A_2+0A_3+1A_4=0$$
$$-C_6H_{12}+C_5H_9CH_3=0 \qquad -0A_1-0A_2-1A_3+1A_4=0$$

Here A_1 stands for C_6H_6, A_2 for H_2, A_3 for C_6H_{12}, and A_4 for $C_5H_9CH_3$. In the right-hand equations, all the components of the reaction mixture are present.

The matrix of the stoichiometric coefficients is as follows:

$$\underline{\nu}=\begin{vmatrix} A_1 & A_2 & A_3 & A_4 \\ -1 & -3 & 1 & 0 \\ -1 & -3 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{vmatrix}$$

We determine the rank of this matrix by the procedure described above. It should be noted that operation (a) does not have to be performed with the first row because the first diagonal element is —1. Subtracting the first row from the second one (subtraction from the third row is not needed because its first element is zero), i.e. performing operation (b), we obtain a matrix with zeros in the first elements of the second and third rows. Next, by performing operations (a) and (b) with the third row (or by simply adding the second and third rows), we find a matrix in which one of the rows consists of zeros. These operations are shown below:

$$\begin{vmatrix} -1 & -3 & +1 & 0 \\ -1 & -3 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{vmatrix} \xrightarrow[\text{first row from second one}]{\text{subtraction of}} \begin{vmatrix} -1 & -3 & 1 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & -1 & 1 \end{vmatrix} \xrightarrow[\text{second row from third one}]{\text{subtraction of}}$$

$$\rightarrow \begin{vmatrix} -1 & -3 & 1 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 \end{vmatrix}$$

The rank of the matrix of the stoichiometric coefficients equals two. Consequently, one of the initial three stoichiometric equations is a dependent one and when analysing the complex equilibrium one should use only two reactions and, accordingly, two equilibrium constants.

The considered procedure is convenient in that the rows of the final matrix (with zero elements) can be employed for writing the set of linearly independent stoichiometric equations, i.e. simultaneously writing the system of reactions that will be linearly independent. For instance, in the considered example, the two significant rows of the last matrix allow us to write the following linearly independent equations that can be used to calculate equilibrium:

$$-C_6H_6-3H_2+C_6H_{12}=0$$
$$-C_6H_{12}+C_5H_9CH_3=0$$

In this example, it is quite simple to establish the dependence of one of the three reactions. But in many cases when the number of proceeding reactions is significant, only analysis of the matrix of stoichiometric coefficients enables one to determine the number and form of the independent reactions. For example, the combustion of hydrogen in the air at high temperatures is described by more than 20 elementary reactions, and one is not able to determine which of them are independent without thorough analysis.

Let us consider a more involved example—the platforming of petrol fractions. Investigation of this process reveals that the proceeding of the following reversible reactions is possible: the isomerization of normal alkanes (Alk) to isoalkanes (IA) and of six-membered cycloalkanes (CA_6) to five-membered ones (CA_5),

the cyclization of the normal and isoalkanes to five- and six-membered cycloalkanes with the evolution of one mole of hydrogen, and the dehydrogenation of the five- and six-membered cycloalkanes to aromatics (A) with the evolution of three moles of hydrogen so that the equations of the proceeding reactions are as follows:

$$-\mathrm{Alk} + \mathrm{IA} = 0 \quad (1) \qquad -\mathrm{IA} + \mathrm{CA}_6 + \mathrm{H}_2 = 0 \quad (5)$$

$$-\mathrm{Alk} + \mathrm{CA}_6 + \mathrm{H}_2 = 0 \quad (2) \qquad -\mathrm{CA}_6 + \mathrm{CA}_5 = 0 \quad (6)$$

$$-\mathrm{Alk} + \mathrm{CA}_5 + \mathrm{H}_2 = 0 \quad (3) \qquad -\mathrm{CA}_5 + \mathrm{A} + 3\mathrm{H}_2 = 0 \quad (7)$$

$$-\mathrm{IA} + \mathrm{CA}_5 + \mathrm{H}_2 = 0 \quad (4) \qquad -\mathrm{CA}_6 + \mathrm{A} + 3\mathrm{H}_2 = 0 \quad (8)$$

To determine the number and form of the independent equations, let us use the described procedure of transforming the matrix of stoichiometric coefficients, which has the following form:

No. of reaction	Stoichiometric coefficients of reactants					
	Alk	IA	CA_5	CA_6	A	H_2
1	−1	1	0	0	0	0
2	−1	0	1	0	0	1
3	−1	0	0	1	0	1
4	0	−1	1	0	0	1
5	0	−1	0	1	0	1
6	0	0	−1	1	0	0
7	0	0	−1	0	1	3
8	0	0	0	−1	1	3

By subtracting the first row from the second and third ones in this matrix, we obtain a matrix with zero elements in the first column from the second to the last row:

$$\begin{vmatrix} -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 & 0 & 1 \\ 0 & -1 & 1 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 & 0 & 1 \\ 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 3 \\ 0 & 0 & 0 & -1 & 1 & 3 \end{vmatrix}$$

In the latter matrix, the second and fourth rows, and also the third and fifth rows are identical. Therefore, by subtracting the second row from the fourth one and the third from the fifth one, we obtain a new matrix in which the fourth and fifth rows contain only zero elements. This allows us to exclude these two lines from the subsequent treatment and further simplify the new matrix containing six rows:

$$\begin{vmatrix} -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 & 0 & 1 \\ 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 3 \\ 0 & 0 & 0 & -1 & 1 & 3 \end{vmatrix}$$

Now by subtracting the second row from the third one, we obtain a matrix with identical third and fourth rows. We therefore exclude the fourth row and perform

a new transformation:

$$\begin{vmatrix} -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 1 \\ 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 3 \\ 0 & 0 & 0 & -1 & 1 & 3 \end{vmatrix} \rightarrow \begin{vmatrix} -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 1 \\ 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 3 \\ 0 & 0 & 0 & -1 & 1 & 3 \end{vmatrix}$$

By excluding one of the coinciding rows (fourth or fifth), we obtain the final matrix of rank four. The four stoichiometric equations determining equilibrium in the system being considered can be written on the basis of the final matrix as follows:

$$-\mathrm{Alk} + \mathrm{IA} = 0, \quad -\mathrm{IA} + \mathrm{CA}_5 + \mathrm{H}_2 = 0, \quad -\mathrm{CA}_5 + \mathrm{CA}_6 = 0,$$
$$-\mathrm{CA}_6 + \mathrm{A} + 3\mathrm{H}_2 = 0$$

The analysis of equilibrium with the participation of four reactions is clearly much simpler than for eight reactions. This is why the analysis of complex equilibrium is often begun with the determination of the independent reactions.

If, on the other hand, the number of reactions is very large (several scores), the determination of the linearly independent ones among them simplifies the calculations only insignificantly. In this case, one can employ the approach dealt with below that is based on the minimization of the Gibbs (Helmholtz) energy of the system determined from the number of moles and the chemical potentials of the reactants.

The following circumstance must be stressed. Although the number of independent reactions is less than (or equal to) the total number of reactions, namely, $p_1 \leqslant p$, all the components of the reaction mixture participate in the independent reactions. Therefore all the n reactants are found both in the p total and in the p_1 independent stoichiometric equations. When studying the change in the numbers of components in the course of a process up to the achievement of equilibrium (kinetic analysis), all the p reactions proceeding in the system must be taken into consideration.

3.2. Determining the Concentrations of Complex Reaction Components with the Use of Chemical Variables

Assume that a complex reaction consisting of p simple ones proceeds in a system, and only p_1 of them are independent. To determine the equilibrium concentrations of all n reactants, we can write p_1 algebraic equations relating the equilibrium constants of the independent simple reactions (these constants are known from thermodynamic calculations) and the equilibrium concentrations. Such a system of equations will enable us to determine only p_1 concentrations, and below we shall see how all n concentrations can be determined for a complex reaction.

In essence, we encountered a similar situation for a simple reaction. In that case (see Sec. 1.7), it was convenient to determine a new variable from the law of mass action, namely, the degree of conversion, in terms of which we preliminarily expressed the concentrations. It is less convenient to use the degree of conversion for a complex reaction because the same substance can participate as the only reactant in several reactions.

To characterize the degree of conversion of substances by a reaction $\sum_i \nu_i A_i = 0$, one can also use the chemical variable λ determining the fraction of a substance relative to its stoichiometric amount that has reacted or has been formed in this reaction. If the magnitude of the change in the number of moles of substance i from the initial one ($m_{i,0}$) to the equilibrium one (m_i) is related to its stoichiometric coefficient ν_i, then this ratio (the chemical variable λ)

$$\lambda = |m_1 - m_{10}| / |\nu_1| = |m_2 - m_{20}| / |\nu_2| = \ldots$$
$$= |m_i - m_{i,0}| / |\nu_i| = |\Delta m_i| / |\nu_i|$$

as follows from stoichiometry, does not depend on i and is the same for all the components. The change in the number of moles of each component can be expressed in terms of the number of moles of another component or in terms of the quantity λ:

$$\Delta m_i = \frac{\nu_i}{\nu_1} \Delta m_1 = \nu_i \lambda; \quad m_i = m_{i,0} + \frac{\nu_i}{\nu_1}(m_1 - m_{10}) = m_{i,0} + \nu_i \lambda$$

When dealing with a complex reaction, we can also introduce chemical variables for each simple reaction. Thus, for the reaction j, namely, $\sum_i \nu_{ij} A_i = 0$, we introduce the variable

$$\lambda_j = \frac{m'_{1j} - m_{10}}{\nu_{1j}} = \frac{m'_{2j} - m_{20}}{\nu_{2j}} = \ldots = \frac{m'_{ij} - m_{i,0}}{\nu_{ij}} = \frac{\Delta m'_{ij}}{\nu_{ij}}$$

Here $m'_{ij} - m_{i,0}$ is the absolute change in the number of moles of substance i because of the j-th reaction.

If, however, substance i participates in several simple steps, it is difficult to determine m'_{ij}. Experiments and calculations allow us to find the number of moles of i in a system obtained owing to the participation of this substance in all the simple steps: $m_i = \sum_j m'_{ij}$.

It is therefore convenient to employ the chemical variable λ_j (in contrast to λ when only one reaction proceeds in a system) only for such complex equilibria when for each simple reaction there is at least one substance participating only in this reaction or for each reaction j there is substance k for which $m_k = m'_{kj}$. This may seem to be a particular case at first sight. However, it is realized for a large number of real situations. Quite rare exceptions are complex reactions in whose simple steps the same set of substances react, but

with different stoichiometric coefficients, for example, with the steps $A_1 + A_2 \rightarrow A_3 + A_4$ and $A_1 + A_2 \rightarrow 2A_3$. Let us therefore consider the use of λ_j for calculating the equilibrium compositions of complex reactions.

For each i-th component of a complex reaction, the change in its mass in the j-th step is $\Delta m'_{ij} = \nu_{ij}\lambda_j$, while the total change in a complex reaction including p simple ones is

$$\Delta m_i = \sum_j \Delta m_{ij} = \sum_j \nu_{ij}\lambda_j$$

Consequently, for an equilibrium mixture, we can express the number of moles of each i-th component in terms of λ_j:

$$m_i = m_{i,0} - \sum_j \nu_{ij}\lambda_j$$

We can also express in terms of λ_j the sum of the moles of all the components:

$$\sum_i m_i = \sum_i m_{i,0} - \sum_i \left(\sum_j \nu_{ij}\lambda_j\right)$$

the mole fraction of each component:

$$x_i = \frac{m_{i,0} - \sum_j \nu_{ij}\lambda_j}{\sum_i m_{i,0} - \sum_i \left(\sum_j \nu_{ij}\lambda_j\right)}$$

and the equilibrium constant K_{x_j} for any reaction j:

$$K_{x_j} = \prod_i {}_j \left[\frac{m_{i,0} - \sum_j \nu_{ij}\lambda_j}{\sum_i m_{i,0} - \sum_i \left(\sum_j \nu_{ij}\lambda_j\right)}\right]^{-\nu_{ij}}$$

(it is assumed here that ν_{ij} for the reactants are positive and for the products are negative). If we introduce the vectors $\mathbf{m}_0$ of the initial composition of the mixture and λ of the chemical variables, then the equation of the law of mass action for independent reactions forms a normal system of equations:

$$\left.\begin{aligned} K_{x_1} &= \varphi_1(\mathbf{m}_0, \lambda) \\ K_{x_2} &= \varphi_2(\mathbf{m}_0, \lambda) \\ &\cdots\cdots\cdots \\ K_{x_p} &= \varphi_p(\mathbf{m}_0, \lambda) \end{aligned}\right\} \qquad (3.2)$$

This system contains p equations and the same number of unknowns λ_j. Its solution allows us to determine the set of equilibrium quantities $\lambda_1, \ldots, \lambda_p$, and from it m_i and x_i for each component.

Let us stop to consider one aspect of the use of system (3.2) which a number of investigations have been devoted to. Since $\varphi_1, \ldots, \varphi_p$ are generally non-linear functions of $\lambda_1, \ldots, \lambda_p$, system (3.2) can have a number of solutions, i.e. sets of $\lambda_1, \ldots, \lambda_p$. The question arises whether several equilibrium compositions are possible for a complex reaction conducted with the same initial mixture and at a constant temperature. Without delving into the content of the performed investigations, it should be noted that in all of them it is shown that there can exist only one set of $\lambda_1, \ldots, \lambda_p$ having a physical meaning (all the λ_j's are real and non-negative quantities), i.e. only one equilibrium state. This is a result of the fact that a minimum of the Helmholtz energy (at T, v = const) or Gibbs energy (at T, p = const) corresponds to equilibrium, while the partial derivatives of A or G with respect to the concentration of any component are monotonic functions [14].

It should now be stressed that when calculating the composition of an equilibrium mixture from p equations of the law of mass action with n unknown concentrations, we can also employ other approaches besides the introduction of the chemical variables $\lambda_1, \ldots, \ldots, \lambda_p$. For example, the following approach is often used. For p independent reactions, we choose p components participating in them that are key components. We express the concentrations of all the other components in terms of the concentrations of the key ones and convert the system of p equations with n unknowns to a normal system of p equations with the same number of unknowns. The relation between the concentrations of the components is given above.

For purposes of illustration, at the conclusion of this section, we shall consider the transition to a normal system of equations when calculating the equilibrium composition of the complex reaction of benzene hydroisomerization. Since, as has been shown above, this reaction is characterized by two independent simple steps, for example,

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12} \text{ and } C_6H_{12} \rightarrow C_5H_9CH_3$$

then by introducing two chemical variables for these steps (λ_1 and λ_2, respectively), we find:

for the masses of the components

$$m(C_6H_6) = m_0(C_6H_6) - \lambda_1,\ m(H_2) = m_0(H_2) - 3\lambda_1,$$

$$m(C_6H_{12}) = m_0(C_6H_{12}) + \lambda_1 - \lambda_2$$

$$m(C_5H_9CH_3) = m_0(C_5H_9CH_3) + \lambda_2,\ \sum m_i = \sum m_{0,i} - 3\lambda_1$$

for the mole fractions of the components

$$x(C_6H_6) = \frac{m_0(C_6H_6) - \lambda_2}{\sum m_{0,i} - 3\lambda_1}, \quad x(H_2) = \frac{m_0(H_2) - 3\lambda_1}{\sum m_{0,i} - 3\lambda_1}$$

$$x(C_6H_{12}) = \frac{m_0(C_6H_{12}) + \lambda_1 - \lambda_2}{\sum m_{0,i} - 3\lambda_1}, \quad x(C_5H_9CH_3) = \frac{m_0(C_5H_9CH_3) + \lambda_2}{\sum m_{0,i} - 3\lambda_1}$$

for the equilibrium constants

$$\left.\begin{aligned} K_{x_1} &= \frac{x\,(C_6H_{12})}{x\,(C_6H_6)\,x^3\,(H_2)} = \frac{[m_0\,(C_6H_{12})+\lambda_1-\lambda_2]\left(\sum m_{0,i}-3\lambda_1\right)^3}{[m_0\,(C_6H_6)-\lambda_1]\,[m_0\,(H_2)-3\lambda_1]^3} \\ K_{x_2} &= \frac{x\,(C_5H_9CH_3)}{x\,(C_6H_{12})} = \frac{m_0\,(C_5H_9CH_3)+\lambda_2}{m_0\,(C_6H_{12})+\lambda_1-\lambda_2} \end{aligned}\right\}$$

Solution of the last system with given values of $m_{0,i}$ and known values of K_{x_1} and K_{x_2} enables us to determine λ_1 and λ_2, and from them the amounts m_i and mole fractions x_i of the components in the equilibrium mixture. It should be noted that although the system of equations relating the equilibrium constants and the chemical variables is of the fourth order, it has only one solution with a physical meaning, namely, with λ_1 and λ_2 real and non-negative.

Another possible procedure for calculations employs the masses of the key components. We choose as the key components benzene (it participates only in the first reaction) and methylcyclopentane (it participates only in the second reaction). Therefore, in accordance with the above relations, we have:

$$m(H_2) = m_0(H_2) - 3m_0(C_6H_6) + 3m(C_6H_6)$$

$$m(C_6H_{12}) = m_0(C_6H_{12}) + m_0(C_6H_6) + m_0(C_5H_9CH_3) - m(C_6H_6) - m(C_5H_9CH_3)$$

$$\sum m_i = \sum m_{0,i} - 3m_0(C_6H_6) + 3m(C_6H_6)$$

In these equations, the masses of the components are expressed in terms of two variables—the masses of the key substances $m(C_6H_6)$ and $m(C_5H_9CH_3)$. If we further express the mole fractions of the components in terms of the same variables, and then the equilibrium constants in terms of the mole fractions, we again obtain two equations (for K_{x_1} and K_{x_2}) with two unknowns, namely, $m(C_6H_6)$ and $m(C_5H_9CH_3)$.

We have already noted that other procedures can also be followed for going over to a normal system of equations. It must be indicated that even in this quite simple case (two simple reactions and four reactants), the solution of system (3.2) is a quite involved problem as regards calculations.

3.3. On Methods of Solving Systems of Algebraic Equations in Calculations of the Equilibrium Compositions of Complex Reactions

It is clear from the above that for p independent reactions we can write p equations for the equilibrium constants that contain the same number of unknowns, for example, system (3.2). Such a system can be solved analytically only in rare cases. Thus, an analytical solution has been obtained for isomerization reactions (see Chap. 6). In general, however, for finding the roots of a system of non-linear algebraic equations, we have to resort to search operations with the use of a computer. Such procedures as applied to the tasks of chemical technology are treated in [13, 15].

Search operations, and, accordingly, the methods of finding the equilibrium compositions from systems of the type of (3.2) can be di-

vided into two main groups: (1) direct search, when an iteration procedure is used to find directly a solution of system (3.2), and (2) indirect search, when we use well developed and sufficiently universal methods of finding the extremum of a function Φ of many variables. Here we must formulate a function of the compositions $\Phi(x_1, \ldots, x_p)$ such that the equilibrium composition $x_1, \ldots, x_p$ would determine the extremum of this function.

The methods of direct search are quite complicated in practical realization. For example, assuming x in the following to stand for a variable quantity (and not for the mole fraction), the system of algebraic equations

$$\left.\begin{array}{l} f_1(x_1, \ldots, x_p) = 0 \\ \cdots\cdots\cdots\cdots \\ f_p(x_1, \ldots, x_p) = 0 \end{array}\right\} \tag{3.3}$$

can be solved by a number of iteration procedures [13, 15], but each of them can be applied only in a limited sphere of conditions making it possible to rapidly transfer a "poor" solution to a good one by an iteration process. Outside of this sphere, the convergence of the solution will be slow or in general even impossible.

Thus, a well-known procedure of simple iteration is based on a transition from system (3.3) to the following one:

$$\begin{array}{l} x_1 = f_1 + x_1 \\ \cdots\cdots \\ x_p = f_p + x_p \end{array}$$

Next the method of successive approximations is employed. Assume that $x_{10}, \ldots, x_{p,0}$, is the initial "poor" solution . Let us improve it by going over to the solution $x_{11}, \ldots, x_{p,1}$ as follows:

$$\begin{array}{l} x_{11} = f_1(x_{10}, \ldots, x_{p,0}) + x_{10} \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ x_{p,1} = f_p(x_{10}, \ldots, x_{p,0}) + x_{p,0} \end{array}$$

and so on.

But such an iteration process may also diverge, i.e. the solution $x_{11}, \ldots, x_{p,1}$ can be worse than $x_{10}, \ldots, x_{p,0}$. It is not always convenient to use the conditions of convergence of an iteration process even if they can be obtained.

Among the direct procedures, the following complex of operations called the Newton-Raphson method is used quite frequently. Assume that the initial approximations $x_{10}, \ldots, x_{p,0}$ are given; we shall find the corrections $h_1, \ldots, h_p$ improving them. Hence, the follow-

ing equations hold:

$$f_1(x_{10}+h_1, \ldots, x_{p,0}+h_p)=0$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$f_p(x_{10}+h_1, \ldots, x_{p,0}+h_p)=0$$

For small values of $h_1, \ldots, h_p$, we can replace the difference of the functions with the total differential so that for any function f_l we have:

$$\Delta f_l = f_l(x_{10}+h_1, \ldots, x_{p,0}+h_p) - f_l(x_{10}, \ldots, x_{p,0})$$
$$= h_1\left(\frac{\partial f_l}{\partial x_1}\right)_0 + \ldots + h_p\left(\frac{\partial f_l}{\partial x_p}\right)_0 + 0_l(h_1, \ldots, h_p)$$

Here the derivatives $(\partial f_l/\partial x_i)_0$ are taken at the point $x_{10}, \ldots, x_{p,0}$, while the quantity $0_l(h_1, \ldots, h_p)$ is small at small values of $h_1, \ldots, h_p$. Disregarding this quantity, we have

$$f_l(x_{10}, \ldots, x_{p,0}) + h_1\left(\frac{\partial f_l}{\partial x_1}\right)_0 + \ldots + h_p\left(\frac{\partial f_l}{\partial x_p}\right)_0 = 0, \quad l=1, 2, \ldots, p$$

In the last system of equations, it is easy to calculate $f_l(x_{10}, \ldots, x_{p,0})$, $(\partial f_l/\partial x_1)_0, \ldots, (\partial f_l/\partial x_p)_0$, and this system is linear relative to $h_1, \ldots, h_p$. Hence, by solving this system relative to $h_1, \ldots, h_p$, we obtain an improved solution, namely, $x_{11} = x_{10} + h_1, \ldots, x_{p,1} = x_{p,0} + h_p$. Now using $x_{11}, \ldots, x_{p,1}$ as the initial approximation, we repeat the above procedure for a new determination of the improving corrections $h_1, \ldots, h_p$.

The Newton-Raphson method converges well in many cases and is easily programmed. It is often included in the standard software of modern computers. But the volume of calculations when using this method is large. One has to calculate the functions $f_1, \ldots, f_p$ at several points (for the calculation of each of them at the initial point and the numerical calculation of the derivatives) and, moreover, it is necessary to solve a system of linear equations.

Let us consider the numerical solution of the system of equations describing the hydroisomerization of benzene (see the preceding example) by the Newton-Raphson method. Assume that $K_{x_1} = 5$, $K_{x_2} = 1$, $m_0(C_6H_6) = 1$, $m_0(H_2) = 3$, $m_0(C_6H_{12}) = m_0(C_5H_9CH_3) = 0$, $\sum m_{i,0} = 4$. Now we have to determine λ_1 and λ_2 from the system

$$f_1(\lambda_1, \lambda_2) = \frac{(\lambda_1-\lambda_2)(4-3\lambda_1)^3}{(1-\lambda_1)(3-3\lambda_1)^3} - 5 = 0$$

$$f_2(\lambda_1, \lambda_2) = \frac{\lambda_2}{\lambda_1-\lambda_2} - 1 = 0$$

It is clear from the form of this system that $\lambda_1 < 1$ and $\lambda_2 < \lambda_1$. Let us choose as the initial approximation $\lambda_{10} = 0.4$ and $\lambda_{20} = 0.3$. To calculate the derivatives, we shall set the increments $\Delta\lambda_1 = \Delta\lambda_2 = 0.05$ (do not confuse with the improv-

ing corrections h_1 and h_2). We now obtain

$$f_1(0.4,\ 0.3) = -4.37, \quad f_1(0.45,\ 0.3) = -3.87$$

$$f_1(0.4,\ 0.35) = -4.69, \quad \left(\frac{\partial f_1}{\partial \lambda_1}\right)_0 = \frac{-3.87+4.37}{0.05} = 10.0$$

$$\left(\frac{\partial f_1}{\partial \lambda_2}\right)_0 = \frac{-4.69+4.37}{0.05} = -6.4$$

$$f_2(0.4,\ 0.3) = 2, \quad f_2(0.45,\ 0.3) = 1, \quad \left(\frac{\partial f_2}{\partial \lambda_1}\right)_0 = \frac{1-2}{0.05} = -20$$

$$f_2(0.4,\ 0.35) = 6, \quad \left(\frac{\partial f_2}{\partial \lambda_2}\right)_0 = \frac{6-2}{0.05} = 80$$

Consequently, we shall find the improving corrections by solving the following system of linear equations:

$$-4.37 + 10h_1 - 6.4h_2 = 0$$
$$2 - 20h_1 + 80h_2 = 0$$

We obtain $h_1 = 0.5$, $h_2 = 0.1$ and go over to the improved solution:

$$\lambda_{11} = 0.4 + 0.5 = 0.9, \quad \lambda_{21} = 0.3 + 0.1 = 0.4$$

Since the obtained values of the corrections are significant, the iteration process for improving the solution must be continued. We reach the same conclusion by verifying the equality to zero of the right-hand sides of the initial system with the found improved values of λ_{11} and λ_{21}. By continuing the iteration process, we arrive at the point $\lambda_1 = 0.6$ and $\lambda_2 = 0.3$, which is near the true value.

The above example shows that with more complicated equilibria, the computer time needed for the calculations may become appreciable. For this reason, indirect methods have been coming into greater use lately.

The indirect methods are based on a transition from the solution of a system of algebraic equations to a function of many variables combining these equations. For example, if we introduce the following functions:

$$\Phi_1 = \sum_{i=1}^{p} f_i = \Phi_1(x_1,\ \ldots,\ x_p) \text{ or } \Phi_2 = \sum_{i=1}^{p} f_i^2 = \Phi_2(x_1,\ \ldots,\ x_p)$$

the solution of the system of algebraic equations

$$\frac{\partial \Phi}{\partial x_1} = 0, \ \ldots, \ \frac{\partial \Phi}{\partial x_p} = 0$$

will correspond to the minima of these functions. The methods of searching for the extremum of a function of many variables have been developed very well, and their use is simpler than the use of the direct method of search. A variant of the gradient method of search is used most frequently.

In the gradient search of the optimum, the initial presumed composition of the equilibrium mixture is chosen. The subsequent search operations include two steps:

(1) investigation of the function $\Phi(x_1, \ldots, x_p)$ near the chosen initial composition to determine what changes in the composition will reduce the value of Φ. This step establishes the direction of the gradient of the function Φ, i.e. the direction in which the value of Φ changes at the highest rate;

(2) changing of the arguments (the mole fractions of the components, the values of the equilibrium conversions for each reaction) ensuring a change in the function Φ in the direction of the gradient and the approach to the extremal (minimal) point.

Let us consider the carrying out of these two steps for a function of many variables of the general form $\Phi = \Phi(x_1, \ldots, x_p)$. If near the initial point we approximate the complex relation $\Phi = \Phi(x_1, \ldots, x_p)$ by the linear equation

$$\Phi = b_0 + b_1x_1 + \ldots + b_px_p$$

the coefficients b will show how to change $x_1, \ldots, x_p$ to lower the value of Φ. If the coordinates of the initial point are $x_{10}, \ldots, x_{p,0}$ and at the given values of $x_1, \ldots, x_p$ we can calculate the value of Φ, then the coefficients b are easy to determine from the values of Φ for the following sets:

$$\Phi_0(x_{10}, \ldots, x_{p,0}), \quad \Phi_1(x_{10} + \Delta x_1, x_{20}, \ldots, x_{p,0})$$
$$\Phi_2(x_{10}, x_{20} + \Delta x_2, x_{30}, \ldots, x_{p,0}), \ldots, \Phi_p(x_{10}, x_{20}, \ldots, x_{p,0} + \Delta x_p)$$

We shall now compile a system of equations:

$$\begin{aligned}
\Phi_0 &= b_0 + b_1x_{10} + \ldots + b_px_{p,0} \\
\Phi_1 &= b_0 + b_1(x_{10} + \Delta x_1) + b_2x_{20} + \ldots + b_px_{p,0} \\
\Phi_2 &= b_0 + b_1x_{10} + b_2(x_{20} + \Delta x_2) + \ldots + b_px_{p,0} \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
\Phi_p &= b_0 + b_1x_{10} + \ldots + b_p(x_{p,0} + \Delta_{x_p})
\end{aligned}$$

We determine the coefficients b from the obvious relations:

$$\Phi_j - \Phi_0 = b_j\Delta x_j \text{ or } b_j = \frac{\Phi_j - \Phi_0}{\Delta x_j} = \frac{\Delta\Phi_j}{\Delta x_j}, \quad j = 1, 2, \ldots, p$$

It is clear that the approximation of the complex non-linear relation $\Phi(x_1, \ldots, x_p)$ by a simple linear equation is correct in the general case only with small changes in Δx_j. The skill of an investigator or programmer consists in being able to choose such appreciable changes Δx_j at which the linear approximation will be sufficiently accurate.

In a number of variants of the gradient method, non-linear approximation is resorted to, for example, approximation of the function $\Phi(x_1, \ldots, x_p)$ by a second-order equation. Here, however, the number of coefficients b to be determined sharply grows, which re-

sults in a larger volume of calculations. This is why preference is given to the method of linear approximation.

When moving along a gradient, we approach the maximum, and when moving along an antigradient, the minimum of the function $\Phi(x_1, \ldots, x_p)$. Changes in each of the x_j's by the amount $\Delta x_{j,\mathrm{gr}}$ proportional to b_j will correspond to the greatest change in Φ_j; here $\Delta x_{j,\mathrm{gr}} = b_j \times C$, where C is an arbitrary constant parameter, the same for all the j's. It is easy to see that

$$\Delta\Phi_{j,\mathrm{gr}} = \Phi_{j,\mathrm{gr}} - \Phi_0 = b_j \Delta x_{j,\mathrm{gr}}$$

Introducing the approximating expressions of $\Phi_{j,\mathrm{gr}}$ and $\Delta x_{j,\mathrm{gr}}$ into this equation, we find:

$$\Delta\Phi_{\mathrm{gr}} = \sum_j \Delta\Phi_{j,\mathrm{gr}} = \sum_j b_j \Delta x_{j,\mathrm{gr}} = C \sum_j b_j^2$$

A glance at the latter expression reveals that the change in Φ_j is positive at $C > 0$ (movement toward the maximum) and negative at $C < 0$ (movement toward the minimum).

Thus, in movement along a gradient, we must determine numerically the coefficients b_j and then choose the constant parameter C. Next we change each of the x_j's by the value $\Delta x_{j,\mathrm{gr}}$ and check the value of Φ for consecutive sets of $x_1, \ldots, x_p$:

$$x_{10} \pm \Delta x_{1,\mathrm{gr}},\ x_{20} \pm \Delta x_{2,\mathrm{gr}},\ \ldots,\ x_{p,0} \pm \Delta x_{p,\mathrm{gr}}$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$x_{10} \pm k\Delta x_{1,\mathrm{gr}},\ x_{20} \pm k\Delta x_{2,\mathrm{gr}},\ \ldots,\ x_{p,0} \pm k\Delta x_{p,\mathrm{gr}}$$

In this sequence, we choose the set of arguments at which Φ is minimum since the gradient method, like the search methods in general, establishes the direction of movement to an optimum, but fails to establish the position of the optimum in this direction. Only by checking a number of values of Φ in the direction of the gradient or antigradient can we determine the best point. At the found best point, we can determine the new direction of the gradient and move in this direction.

There is a large number of modifications of the gradient method of searching for the extremum of the functions of many variables that take into consideration the "curving" of the gradient surface or the fact that when getting onto a "ridge" ("valley"), one's movement along the gradient is slow and unstable. Data on the application of these methods for calculations of the equilibrium compositions are contained in reviews [14-16].

3.4. Sequence of Calculating Complex Equilibrium by the Traditional Methods

Let us now consider the steps of the traditional determination of the composition of an equilibrium mixture in a complex reaction. They include: (1) determination of the stoichiometric equations of the independent reversible simple reactions, (2) writing the equations of the law of mass action for the independent reactions relating the equilibrium constants to the concentrations (amounts) of the components, (3) the compilation of additional coupling equations of the relation between the concentrations (amounts) of the components or of the relation between the concentrations and the chemical variables; this enables us to obtain a closed system of equations in which the number of equations equals the number of unknown concentrations, and (4) the analytical or numerical solution of the system of equations to find the concentrations (amounts) of the components.

The obtaining of independent stoichiometric equations has been described on a previous page. Having further determined the equilibrium constants for these equations, we retain for further analysis only the simple reactions that under the conditions being studied proceed as reversible ones, i.e. with degrees of conversion substantially differing both from zero and from 100%.

The thermodynamic calculations of the equilibrium constants and the writing of the equations of the law of mass action involve no difficulties. We have already stressed that it is convenient to use the constant K_x for gas reactions and K_c for reactions in solutions because in this case the transition to degrees of conversion or chemical variables is simplified.

There is considerable variety in compiling the additional coupling equations. If p reactions with the participation of n substances proceed in a system, to determine the n unknown concentrations we additionally require $n - p$ equations.

The methods of writing these equations by introducing the degree of conversion or the chemical variables have been described earlier. But often a different procedure is employed that does not require the introduction of new variables. It takes into account the constancy of the number of atoms of each element in the reactants. If a molecule of substance A_i contains a_{il} atoms of the l-th chemical element and the number of moles of A_i varies from $m_{i,0}$ (initial mixture) to m_i (equilibrium mixture), we have

$$\sum_i a_{il} m_i = \sum_i a_{il} m_{i,0} \text{ or } \sum_i a_{il} (m_i - m_{i,0}) = 0$$

These conditions are generally sufficient to obtain a closed system of equations.

For instance, in the example of the complex reaction in platforming considered above (see p. 107), for the four independent reactions in an ideal gas mixture we have four equations of the law of mass action in which there are six unknown amounts m_i, namely:

$$K_{x_1} = \frac{x_{\mathrm{IA}}}{x_{\mathrm{Alk}}} = \frac{m_{\mathrm{IA}}}{m_{\mathrm{Alk}}} \qquad K_{x_2} = \frac{x_{\mathrm{CA_5}} x_{\mathrm{H_2}}}{x_{\mathrm{IA}}} = \frac{m_{\mathrm{CA_5}} m_{\mathrm{H_2}}}{m_{\mathrm{IA}} \sum\limits_i m_i}$$

$$K_{x_3} = \frac{x_{\mathrm{CA_6}}}{x_{\mathrm{CA_5}}} = \frac{m_{\mathrm{CA_6}}}{m_{\mathrm{CA_5}}}$$

$$K_{x_4} = \frac{x_{\mathrm{A}} x_{\mathrm{H_2}}^3}{x_{\mathrm{CA_6}}} = \frac{m_{\mathrm{A}} m_{\mathrm{H_2}}^3}{m_{\mathrm{CA_6}} \left(\sum\limits_i m_i\right)^3}$$

where $\sum\limits_i m_i = m_{\mathrm{IA}} + m_{\mathrm{Alk}} + m_{\mathrm{CA_5}} + m_{\mathrm{CA_6}} + m_{\mathrm{A}} + m_{\mathrm{H_2}}$.

We obtain two additional equations from the conditions of a constant number of carbon and hydrogen atoms. If hydrocarbons with six carbon atoms (n-hexane, isohexane, cyclohexane, methylcyclopentane, benzene) are being converted, these equations are as follows:

$$(m_{\mathrm{Alk}} - m_{0,\mathrm{Alk}}) + (m_{\mathrm{IA}} - m_{0,\mathrm{IA}}) + (m_{\mathrm{CA_5}} - m_{0,\mathrm{CA_5}}) + (m_{\mathrm{CA_6}} - m_{0,\mathrm{CA_6}}) + (m_{\mathrm{A}} - m_{0,\mathrm{A}}) = 0$$

$$14\,[(m_{\mathrm{Alk}} - m_{0,\mathrm{Alk}}) + (m_{\mathrm{IA}} - m_{0,\mathrm{IA}})] + 12\,[(m_{\mathrm{CA_5}} - m_{0,\mathrm{CA_5}}) + (m_{\mathrm{CA_6}} - m_{0,\mathrm{CA_6}})] + 6\,(m_{\mathrm{A}} - m_{0,\mathrm{A}}) + 2\,(m_{\mathrm{H_2}} - m_{0,\mathrm{H_2}}) = 0$$

The system of equations with six unknowns is closed (K_{x_i} and $m_{0,i}$ are known) and has a single solution with a physical meaning. We shall note in concluding that the condition of the constancy of the number of atoms of the elements in a chemical reaction $\sum\limits_i \nu_{ij} A_i = 0$ can be written in the form $\sum\limits_i \nu_{ij} a_{il} = 0$. After obtaining a closed system of equations, we are confronted with the task of finding the solution (the degrees of conversion, chemical variables, masses of the components). It should be noted that for isothermal complex reactions of the same type (isomerization, alkylation, disproportionation, etc.), we usually succeed in obtaining analytical solutions. Examples of such solutions are given in the sections devoted to specific reactions.

But if the number of simple reactions is large and they relate to various types (for example, dehydrogenation and isomerization), and also for adiabatic reactions, we have to resort to the search methods treated above, which requires the use of a computer.

3.5. A Universal Method for Determining the Composition of the Equilibrium Mixture of a Complex Reaction — Minimization of the System's Energy

It has been noted that if the number of simple reactions is large, the determination of the independent reactions from among them only insignificantly simplifies the calculations. This is why we can state our approach to the calculation of equilibrium as follows: since in equilibrium the Gibbs energy G (a reaction at T, p = const) or Helmholtz energy A (a reaction at T, v = const) is minimum, we have to find the composition of a mixture ensuring a minimum value of G or A.

Apparently, the expediency of directly using the Gibbs or Helmholtz energy of a system for determining the chemical composition of equilibria was first indicated by Zeldovich [14]. Proceeding from the condition that $G = \sum m_i\mu_i$ and using the condition that the number of atoms of each element is retained in the course of a reaction, he showed that although the equilibrium constants are related to m_i non-linearly, there is only a single set of equilibrium values of m_i having a physical meaning, i.e. he showed the singleness of the state of equilibrium.

Although the condition of equilibrium can be written in the form of a minimum Gibbs (or Helmholtz) energy or in the form of the law of mass action, one should not presume that these forms differ in principle. In both cases, the same general relations of chemical thermodynamics and the same thermodynamic functions of substances are employed. But the method of minimization of G (or A) uses a procedure for finding the solution by a numerical technique in a computer by searching for the minimum of a function of many variables and is programmed so that it does not require the successive carrying out of steps A-D of the traditional approach.

Let us consider a most general system containing k components and r phases, so that m_i^φ is the number of moles of the i-th component in phase φ. For the Gibbs energy of the system, we have $G = G(T, p, m_i^\varphi)$. Since G is an extensive function, when the size of the system is increased k times, $G(T, p, km_i^\varphi) = kG(T, p, m_i^\varphi)$. By introducing the chemical potentials for the system at T, p = const, we have:

$$G = \sum_{i,\varphi} m_i^\varphi \mu_i^\varphi \tag{a}$$

where the chemical potential is determined from the condition

$$\mu_i^\varphi = \left(\frac{\partial G}{\partial m_i^\varphi}\right)_{T,p,m_j} \tag{b}$$

If we equate the differentials of G from Eqs. (a) and (b), we obtain the Gibbs-Duhem equation

$$\sum_{i,\varphi} m_i^\varphi \, d\mu_i^\varphi = 0$$

Some additional conditions are used to analyse equilibrium because not all the m_i's are independent. As indicated above, the number of atoms of each l-th chemical element must remain constant. If the initial system contained b_l atoms, then with a view to the above notation, we have

$$\varphi_l = \sum_\varphi \sum_i a_{li} m_i^\varphi - b_l = 0 \qquad \text{(c)}$$

A similar condition can also be obtained for the charges of the particles if ions participate in a process. In this case, Eq. (c) can be written again for a charge (its number is $l + 1$), but $b_{l+1} = 0$, while $a_{i,l+1}$ is the charge of the i-th substance.

In Eqs. (a) and (b), the masses of the components are independent variables, and conditions (c) are introduced to determine them. When searching for the minimum of the function G using conditions (c), it is good to employ the Lagrange method of undetermined coefficients λ_l. By this method, the function G is replaced with $\Phi = G + \sum_l \lambda_l \varphi_l$. Here the positions of the extremum of Φ and G coincide provided that $\partial\Phi/\partial m_i^\varphi = \partial\Phi/\partial\lambda_l = 0$. By introducing λ_l, we again increase the number of unknowns. Thus, we go over to a search for the minimum of a new function:

$$\Phi = G + \sum_l \lambda_l \left(\sum_{\varphi,i} a_{il} m_i^\varphi - b_i\right) = \sum_{\varphi,i} m_i^\varphi \mu_i^\varphi + \sum_l \lambda_l \left(\sum_{\varphi,i} a_{il} m_i^\varphi - b_l\right)$$

The condition of a minimum of Φ yields:

$$\left.\begin{aligned} &\mu_i^l + \sum_i \lambda_l a_{il} = 0 \\ &\sum_{\varphi,i} a_{il} m_i^\varphi - b_l = 0 \end{aligned}\right\} \qquad \text{(d)}$$

We obtain a system of non-linear equations that must be solved to determine the equilibrium amounts m_i^φ and the Lagrange coefficients λ_l.

But (d) is interesting because the coefficients λ_l do not depend on the form of the phase φ. It follows that the chemical potential μ_i is the same for all phases and, moreover, can explain the physical meaning of λ_l. By inserting (d) into (a), with a view to (c), we find:

$$G = -\sum_i \lambda_l b_l$$

where λ_l is the contribution of the element l to the Gibbs energy of the system.

If the chemical reactions

$$\sum \nu_{ij}^{\varphi} A_i^{\varphi} = 0$$

proceed, then ν_{ij}—the stoichiometric coefficients of the j-th reaction—are chosen so as to preserve the balance by elements. Hence

$$\sum a_{il} \nu_{ij}^{\varphi} = 0 \quad (\nu_{ij}^{\varphi} > 0 \text{ for the products})$$

The conditions of chemical equilibrium give additional relations in the form of the law of mass action:

$$\sum \nu_{ij}^{\varphi} \mu_i^{\varphi} = 0$$

But if it is difficult to establish the kind of the reactions (a complex multiphase multicomponent system), one may not use the equation of chemical equilibrium, but relate the chemical potential of a component to the thermodynamic functions of components given in standard tables.

We shall show how calculations are performed using the method of minimizing the Gibbs energy by taking a simple example of the substances A_1 and A_2. The approach set out below will be featured by the fact that instead of considering the chemical process of obtaining A_2 from A_1 (i.e. the law of mass action), we shall use tabulated data on the logarithms of the equilibrium constants of formation of A_1 and A_2 for our calculations.

Let us consider the reaction of formation of A_i from simple substances L:

$$\sum_l \nu_{il} L_l \rightarrow A_i$$

For this reaction,

$$\Delta G_f = \mu_i - \sum_l \nu_{il} \mu_l \tag{e}$$

Since

$$\mu_i = h_i + RT \ln a_{0i} \equiv \mu_i^{\circ} + RT \ln a_{0i}$$

(where a_{0i} is the activity of A_i), then at arbitrary activities a_{0i} we have:

$$\Delta G_f = \mu_i^{\circ} + RT \ln a_{0i} - \left(\sum_l \nu_{il} \mu_l^{\circ} + \sum_l \nu_{il} RT \ln a_{0l}\right)$$

At equilibrium, $\Delta G_f = 0$, and, therefore,

$$\mu_i^{\circ} - \sum_l \nu_{il} \mu_l^{\circ} = -RT \ln \frac{G_i}{\prod_l a_l^{\nu_{il}}} = -RT \ln K_{a,f,i}$$

Hence,

$$\Delta G_f = -RT \ln K_{a,f,i} + RT \ln \frac{a_{0i}}{\prod_i a_{0l}^{\nu_{il}}} \tag{f}$$

A comparison of (e) and (f) yields

$$\mu_i = -RT \ln K_{a,f,i} + RT \ln \frac{a_{0i}}{\prod_i a_{0l}^{\nu_{il}}} + \sum_l \nu_{il} \mu_l$$

The last two terms do not depend on the composition of the equilibrium mixture.

Now let us write an expression for the Gibbs energy of the system containing A_1 and A_2:

$$G=m_1\mu_1+m_2\mu_2=RT\left(-m_1\ln K_{a,f,1}+m_1\ln\frac{a_{01}}{\prod\limits_l a_{0l}^{\nu_{1l}}}\right.$$

$$\left.+\frac{m_1}{RT}\sum_l \nu_{1l}\mu_l-m_2\ln K_{a,f,2}+m_2\ln\frac{a_{02}}{\prod\limits_l a_{0l}^{\nu_{2l}}}+\frac{m_2}{RT}\sum_l \nu_{2l}\mu_l\right)$$

When seeking the equilibrium composition, this expression has to be supplemented with the conditions of the constancy of the element atoms in the system:

$$\varphi_l=\sum_i \nu_{il}m_i-b_l=0$$

The function being minimized with account taken of the restrictions imposed will be as follows (the Lagrange method of undetermined coefficients has been used):

$$\Phi=G+\sum \lambda_l\varphi_l$$

We shall now consider the case when there is no need to introduce several functions φ. Thus, for a mixture of butane and isobutane, it is in essence a single function $\varphi = m_1 + m_2 - m_0$; $m_0 = m_{01} + m_{02}$. Indeed,

$$4m_1 + 4m_2 - b_l = 0 \text{ (carbon balance)}$$

$$10m_1 + 10m_2 - 2.5b_l = 0 \text{ (hydrogen balance)}$$

$$b_l = 4m_0$$

Let us also consider the reaction of formation of A_i from simple substances in their standard states when $a_{0l} = 1$. Moreover, let the reaction mixture be an ideal gas mixture so that $a_i = x_i = m_i/m_0$. In this case, $K_a = K_x$, consequently

$$\Phi=G+\lambda\varphi=RT\left(-m_1\ln K_{x\,f,1}+m_1\ln\frac{m_1}{m_0}\right.$$

$$+\frac{m_1}{RT}\sum_l \nu_{1l}\mu_l^\circ-m_2\ln K_{x,f,2}+m_2\ln\frac{m_2}{m_0}$$

$$\left.+\frac{m^2}{RT}\sum_l \nu_{2l}\mu_l^\circ\right)+\lambda(m_1+m_2-m_0)$$

At the point of the minimum

$$\frac{\partial\Phi}{\partial m_1}=-RT\ln K_{x\,f,1}+RT\left(\ln\frac{m_1}{m_0}+1\right)+\sum_l \nu_{1l}\mu_l^\circ+\lambda=0 \qquad \text{(g)}$$

$$\frac{\partial\Phi}{\partial m_2}=-RT\ln K_{x,f,2}+RT\left(\ln\frac{m_2}{m_0}+1\right)+\sum_l \nu_{2l}\mu_l^\circ+\lambda=0 \qquad \text{(h)}$$

$$\frac{\partial\Phi}{\partial\lambda}=m_1+m_2-m_0=0$$

Equating expressions (g) and (h) and having in view that $\sum_l \nu_{1l}\mu_l^\circ = \sum_l \nu_{2l}\mu_l^\circ$ (A_1 and A_2 have the same chemical composition), we find:

$$-\ln K_{x,f,1} + \ln \frac{m_1}{m_0} = -\ln K_{x,f,2} + \ln \frac{m_2}{m_0}$$

whence

$$\ln K_{x,f,2} - \ln K_{x,f,1} = \ln \frac{m_2}{m_1}$$

Taking into consideration the condition $m_2 = m_0 - m_1$, we obtain a working equation:

$$\frac{K_{x,f,2}}{K_{x,f,1}} = \frac{m_2}{m_0 - m_2} \tag{3.4}$$

It can be seen that the working equation (3.4) has been obtained without using the constants of chemical equilibrium between the reactants. It can also be obtained by considering the reaction $A_1 \rightarrow A_2$ (the condition $\sum_l \nu_{1l}\mu_l^\circ = \sum_l \nu_{2l}\mu_l^\circ$ presumes that one mole of A_1 yields one mole of A_2). For the reaction being considered,

$$K_x = \frac{m_2}{m_0 - m_2}$$

and

$$K_x = \frac{K_{x,f,2}}{K_{x,f,1}}$$

If three substances A_1, A_2, and A_3 having the same chemical formula reacted, then by analogy with the above treatment, minimization of the Gibbs energy would result in the expressions:

$$-RT \ln K_{x,f,1} + RT\left(\ln \frac{m_1}{m_0} + 1\right) + \sum_l \nu_{1l}\mu_l^\circ + \lambda = 0 \tag{i}$$

$$-RT \ln K_{x,f,2} + RT\left(\ln \frac{m_2}{m_0} + 1\right) + \sum_l \nu_{2l}\mu_l^\circ + \lambda = 0 \tag{j}$$

$$-RT \ln K_{x,f,3} + RT\left(\ln \frac{m_3}{m_0} + 1\right) + \sum_l \nu_{3l}\mu_l^\circ + \lambda = 0 \tag{k}$$

$$m_1 + m_2 + m_3 - m_0 = 0, \quad m_0 = m_{0,1} + m_{0,2} + m_{0,3}$$

Proceeding as previously, i.e. equating expressions (i) and (j), (j) and (k), we find:

$$\frac{K_{x,f,2}}{K_{x,f,1}} = \frac{m_2}{m_1}; \quad \frac{K_{x,f,3}}{K_{x,f,2}} = \frac{m_3}{m_2}; \quad m_1 + m_2 + m_3 = m_0$$

Solution of this system of equations with three unknowns allows us to determine m_1, m_2, and m_3.

In the considered examples, minimization of the Gibbs energy of a system leads to correct expressions in a longer way than the solution of the equations of the law of mass action. But for complex systems

(scores of reactants and reactions), the minimization of the Gibbs or Helmholtz energy of a system will be simpler. Information on the programmes of calculations by the universal method is contained in [14, 16, 17], among others. A programme of calculations using the Fortran IV language is contained in [17, 18].

Chapter 4

Adiabatic Equilibrium Reactions

On preceding pages, we have calculated the equilibrium composition for isothermal reactions. In real technical processes such as platforming, hydrocracking, and the oxidation of fuel in a jet engine, the reactions proceed under conditions close to adiabatic ones. The calculation of the equilibrium composition from the value of the equilibrium constant for an adiabatic reaction is complicated because it is necessary to preliminary determine the temperature of the reaction mixture at the outlet from the apparatus (or at the end of the process), but this temperature, in turn, is determined by the possible degree of conversion. Thus, when calculating adiabatic reactions, one has to use the trial-and-error method to ensure correspondence between the outlet temperatures and the equilibrium composition. The scheme of calculating an adiabatic reaction considered below is suitable for any conditions of its proceeding in through-flow or static apparatuses.

4.1. Simple Reactions

Assume that the following relations have been established for the reaction $\nu_1 A_1 + \nu_2 A_2 + \ldots \rightarrow \nu_1' A_1' + \nu_2' A_2' + \ldots$ (where all the ν's are considered to be positive).

1. The temperature dependence of the heat capacity of each i-th component (at p = const):

$$C_{p,i} = a_i + b_i T + c_i T^2 \tag{4.1}$$

2. The temperature dependence of the heat of a reaction (at p = = const)

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta C_p \, dT = \Delta H_{T_0} + \int_{T_0}^{T} (\Delta a + \Delta b T + \Delta c T^2) \, dT$$

Introducing the notation

$$\Delta H_{T_0} - \Delta a T_0 - \frac{\Delta b}{2} T_0^2 - \frac{\Delta c}{3} T_0^3 \equiv B$$

we obtain

$$\Delta H_T = B + \Delta a T + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{3} T^3 \tag{4.2}$$

3. The temperature dependence of the equilibrium constant (at p = const):

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

With account taken of the dependence of ΔH on T, we obtain:

$$\ln \frac{K_{p,T}}{K_{p,T_0}} = \frac{B}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \frac{\Delta a}{R} \ln \frac{T}{T_0} + \frac{\Delta b}{2R}(T - T_0) + \frac{\Delta c}{6R}(T^2 - T_0^2) \tag{4.3}$$

4. The dependence of the equilibrium constant on the degree of conversion y:

$$K_x = \frac{K_p}{p^{\Delta\nu}} = \frac{1}{\left(1 + \delta_2 + \ldots + \delta_1' + \delta_2' + \ldots + \frac{\Delta\nu}{\nu_1} y\right)^{\Delta\nu}} \times \frac{\prod\limits_{i'} \left(\delta_i' + \frac{\nu_i'}{\nu_1} y\right)^{\nu_i'}}{\prod\limits_{i} \left(\delta_i - \frac{\nu_i}{\nu_1} y\right)^{\nu_i}} \tag{4.4}$$

5. The system of equations (4.1)-(4.4) is used in essence to find ΔH, K_p, and y at the reaction temperature T. When dealing with an adiabatic reaction, we must obtain an additional equation for calculating T. For this purpose, we shall introduce the equation of the heat balance of an adiabatic reaction.

If the initial mixture contained m_0 moles of A_1, and m_i moles of A_i, while $m_0\, dy$ moles of A_1 reacted, then at the heat of the reaction related to one mole, the amount of heat "taken away" by the reaction is

$$\Delta H_T m_0\, dy = \left(-\sum_i m_i C_{p,i}\right) dT$$

The right-hand side of this equation takes into account that the absorbed heat lowers the temperature of the system by dT. The equation has been written for elementary changes in the degree of conversion and temperature because C_p and ΔH are functions of the temperature. Summation on the right-hand side is performed over all the components of the reacting mixture. Here:

$$m_i = m_0\left(\frac{m_{0i}}{m_0} + \frac{\nu_i}{\nu_1} y\right) = m_0\left(\delta_i + \frac{\nu_i}{\nu_1} y\right)$$

We shall stress that in the latter expression the stoichiometric coefficients ν_i for the products are positive, for the reactants are negative, and for diluents (inert substances) are zero.

Therefore, the equation of the heat balance can be written as

$$\Delta H_T \frac{dy}{dT} = -\sum_i C_{p,i} \left(\delta_i + \frac{\nu_i}{\nu_1} y\right) \tag{4.5}$$

We have thus obtained a system of non-linear equations (4.1)-(4.5) in which the number of unknowns equals the number of equations. Its solution allows us to find $C_{p,i}$, ΔH_T, K_p, y, and T satisfying the above scheme.

Although the system (4.1)-(4.5) is non-linear, it has only one solution with a physical meaning. This follows from the fact that at any temperature there is only one physical state of a system ensuring a minimum Gibbs energy, i.e. the condition of equilibrium [3]. The solution cannot be obtained analytically in the general case, and one has to use search methods. Such methods involving the use of computers are treated in [8, 15].

The search of a solution for the system (4.1)-(4.5) is quite involved. Therefore, in practical calculations, certain procedures are used that simplify the search for a solution. We shall characterize some of them below.

4.2. Reaction with a Small Temperature Change

To appraise the region near which this temperature is, it is convenient to disregard the effect of the temperature on $C_{p,i}$ and ΔH as an approximation. Now system (4.1)-(4.5) is simplified, and T is selected using the algebraic system

$$\left.\begin{aligned} K_{p,T} &= K_{p,T_0} \exp\left[\frac{\Delta H_{T_0}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \\ y &= \varphi(K_p) \\ \Delta H_{T_0} y &= -\sum_i C_{p,i}\left(\delta_i - \frac{\nu_i}{\nu_1} y\right)(T - T_0) \end{aligned}\right\} \tag{4.6}$$

For specific reactions, the solution can be found analytically or by simple trial-and-error in a number of cases (see the example below). If T_0 and T do not differ very appreciably (by not more than 100 K), the found approximate solution will be sufficiently close to the exact one and will require no further refinement. This case is realized for processes of mutual transitions of hydrocarbons.

Let us illustrate how the calculations are performed. Assume that the reaction $A_1 \rightarrow A_1'$ proceeds in an ideal gas phase, and only A_1 is present in the initial mixture. We first find an approximate solution assuming that C_{p,A_1}, $C_{p,A_1'}$, and ΔH do not depend on the temperature. For the given case, we have (K_p =

$= K_x$):

$$K_{x,T} = K_{x,T_0} \exp\left[\frac{\Delta H_{T_0}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$$K_{x,T} = \frac{y}{1-y}\ ;\quad y = \frac{K_{x,T}}{1+K_{x,T}}$$

$$\Delta H_{T_0} y = -[C_{p,A_1}(1-y) + C_{p,A_1'} y](T - T_0)$$

We express y in terms of K_{x,T_0} and obtain an implicit equation for determining T:

$$\Delta H_{T_0} K_{x,T_0} \exp\left[\frac{\Delta H_{T_0}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$
$$= \left\{C_{p,A_1} + C_{p,A_1'} K_{x,T_0} \exp\left[\frac{\Delta H_{T_0}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\right\}(T_0 - T)$$

We determine the quantities for the temperature T_0 in this equation, namely, the heat capacities C_{p,A_1} and $C_{p,A_1'}$, the heat of the reaction ΔH, and the equilibrium constant K_x from the data of standard thermodynamic tables. For example, for $T_0 = 500$ K, we have found $C_{p,A_1} = 80$ J/(mol·K), $C_{p,A_1'} = 70$ J/(mol × × K), $\Delta H_{T_0} = -5400$ J/mol, and $K_{x,T_0} = 0.80$. Hence, for finding T, we obtain the implicit equation

$$-5400 \times 0.8 \exp\left[-\frac{5400}{8.31}\left(\frac{1}{500} - \frac{1}{T}\right)\right]$$
$$= \left\{80 + 70 \times 0.80 \exp\left[-\frac{5400}{8.31}\left(\frac{1}{500} - \frac{1}{T}\right)\right]\right\}(500 - T)$$

Let us denote the right-hand side of this equation by $-f_1(T)$ and the left-hand side by $-f_2(T)$. The values of these functions are given below for various temperatures T:

T, K	501	510	515	520	524	525
$-f_1(T)$	11 967	3478	3200	2979	2834	2801
$-f_2(T)$	235	1248	1822	2372	2801	2908

We can find the solution graphically from these data by plotting lines of $-f_1(T)$ and $-f_2(T)$ versus T and determining the point of their intersection, when $-f_1(T) = -f_2(T)$. The value of $T \approx 524$ K corresponds to this point. At 524 K, we have $K_x = 0.75$ and $y = 0.43$.

Thus, when conducting the adiabatic reaction, the equilibrium temperature is 524 K, and the equilibrium degree of conversion is 0.43.

Since T_0 and T (500 and 524 K, respectively) differ insignificantly, there is no need to refine this solution. But if the difference were more significant, the calculations could be repeated by substituting ΔH_T for ΔH_{T_0}.

At large values of $|\Delta H|$ (processes of partial and complete oxidation, deep hydrocracking), the difference between T_0 and T can reach several hundreds, and sometimes thousands of kelvins. In such cases, it is convenient to use the found approximate solution as the angular point of a segment for scanning (see [8]).

4.3. Reaction with a Considerable Temperature Change and a Degree of Conversion Close to Unity (the Equilibrium Adiabatic Temperature of Irreversible Combustion)

When calculating fuel combustion processes, one must determine the amount of heat evolved, as well as the temperature and composition of the combustion products. It is sometimes assumed in these calculations that all the evolved heat of combustion goes to heat the reaction mixture, i.e. that the reaction proceeds adiabatically. Owing to the high evolution of heat in combustion, the temperature of a system rises by a thousand or even several thousands of Kelvins, therefore we cannot ignore the effect of the temperature on C_p and ΔH as we did in the examples of the preceding section. For example, the complete combustion of methane in oxygen to molecular products raises the temperature to about 3000 K, and in air to about 2000 K.

If the stoichiometric equation of a combustion reaction is known and the reaction proceeds irreversibly, the adiabatic temperature of combustion can be calculated by solving the system of equations of the heat balance and the temperature dependence of ΔH. Assume that the mole fraction x_i of the i-th component can be expressed in terms of the content in the mixture of the component on which measurement of the heat of combustion* ΔH_c is based (the subscript of this component is "1").

Hence, the system (4.1)-(4.5) transforms into the following one:

$$\left.\begin{aligned} \Delta H_{c,T} &= \Delta H_{c,T_0} + \int_{T_0}^{T} \Delta C_p \, dT \\ \frac{dx_1}{dT} &= -\frac{\sum_i x_i C_{p,i}}{\Delta H_{c,T}} \end{aligned}\right\} \tag{4.7}$$

These equations can be combined:

$$\frac{dx_1}{dT} = -\frac{\sum_i x_i C_{p,i}}{\Delta H_{c,T_0} + \int_{T_0}^{T} \Delta C_p \, dT} \tag{4.8}$$

Numerical or analytical integration of Eq. (4.8) within the limits from x_1 to 0 for the mole fraction and from T_0 to T for the temperature enables one to determine T.

* In the preceding section, ΔH_c stood for the heat of combustion of a substance to its higher oxides (for example, CO_2, H_2O). In high-temperature combustion, radicals (such as $\dot{H}$, $\dot{O}H$) can be reaction products. In Secs. 4.3 and 4.4, ΔH_c will designate the heat of any combustion reaction.

But one can also use the iteration procedure that simplifies the calculations. This procedure includes (1) calculation of the adiabatic temperature for the irreversible process from the equation of the heat balance for the "mean" heat of combustion, (2) checking of the degree of conversion at this temperature, and (3) repetition of the calculations for the found degree of conversion and the new "mean" heat of combustion.

Let us consider the following example to illustrate the application of this procedure. Assume that we have to calculate the temperature of combustion of H_2 in air [80% (mole) N_2, 20% (mole) O_2], a three-fold excess of oxygen being used. This signifies that there are 1.5 moles of O_2 and six moles of N_2 per mole of H_2. At 298 K, the heat of combustion of H_2 with the formation of one mole of gaseous water $\Delta H_c^\circ = -241.835$ kJ/mol, the equilibrium constant of this reaction is $K_a \approx K_x = 1 \times 10^{40}$, while the temperature dependence of $C_{p,i}^\circ$ and $\Delta C_{p,i}$ is as follows [$C_{p,i}^\circ$ is in J/(mol·K)]:

$$C_p^\circ\,(O_2) = 25.70 + 12.98 \times 10^{-3}T$$
$$C_p^\circ\,(N_2) = 27.30 + 5.23 \times 10^{-3}T$$
$$C_p^\circ\,(H_2) = 29.07 - 0.50 \times 10^{-3}T$$
$$C_p^\circ\,[H_2O\,(g)] = 30.36 + 9.58 \times 10^{-3}T$$
$$\Delta C_p^\circ = -11.56 + 3.59 \times 10^{-3}T$$

According to the conditions of our example, the amounts of components (in moles) are as follows:

Components	N_2	O_2	H_2	H_2O	Total
Beginning of process (in)	6.0	1.5	1.0	0	8.5
End of process (out)	6.0	1.0	0	1.0	8.0

Let us appraise the heating temperature. We assume that the heat of the reaction does not change with the temperature and that the final mixture of products is heated. Hence

$$\Delta H_c^\circ = -\int_{298}^{T} (C_p^\circ)_{out}\,dT$$

Since

$$(C_p^\circ)_{out} = 6C_p^\circ\,(N_2) + C_p^\circ\,(O_2) + C_p^\circ\,(H_2O) = 219.86 + 53.94 \times 10^{-3}T \text{ J/K}$$

we have

$$-241\,835 = -\left[219.86\,(T - 298) + \frac{53.94 \times 10^{-3}}{2}\,(T^2 - 298^2)\right]$$

From this quadratic equation, we find $T = 1215$ K. We find the heat of combustion at 1215 K:

$$\Delta H_{c,1215}^\circ = -241\,835 - 11.56\,(1215 - 298) + \frac{3.59 \times 10^{-3}}{2}\,(1215^2 - 298^2) = -249\,954 \text{ J}$$

Hence, the heat of the reaction changes insignificantly, and we can repeat the calculations of the adiabatic temperature of combustion by using the "mean" heat of combustion $\Delta H_c^\circ = -246\,000$ J. Repeated calculations yield $T = 1220$ K. Let us now find the equilibrium constant at 1220 K. We have:

$$\ln \frac{K_{x,1220}}{K_{x,298}} = \int_{298}^{1220} \frac{-241\,835 - 11.56\,(T - 298) - (3.59 \times 10^{-3}/2)\,(T^2 - 298^2)}{RT^2}\,dT$$

The calculations give $K_{x,1300} = 6.2 \times 10^6$.

We now find the equilibrium degree of conversion of hydrogen. The number of moles in the equilibrium mixture is:

$$m(H_2) = 1 - y, \quad m(O_2) = 1.5 - 0.5y, \quad m(H_2O) = y, \quad \sum m_i = 8.5 - 0.5y.$$

Consequently,

$$K_x = \frac{y(8.5-0.5y)^{1/2}}{(1-y)(1.5-0.5y)^{1/2}}$$

A value of $y = 0.999\,998$ corresponds to $K_x = 6.2 \times 10^6$, i.e. the reaction is virtually irreversible.

4.4. Reaction with a Considerable Temperature Change (Equilibrium Adiabatic Temperature of Reversible Combustion)

For these reactions too, we can use simplified calculation procedures enabling us to obtain satisfactory estimates of the accurate solution of the system (4.1)-(4.5). Below we shall consider one of the ways of finding an approximate solution.

1. Initially, assuming the heat of combustion to be constant, we estimate the temperature of adiabatic heating of the products of complete combustion. If m_i is the number of moles of the i-th component in the products of complete combustion (m_i is evaluated from the initial number of moles $m_{0,i}$ and the stoichiometric equation), then upon the combustion of $m_{0,1}$ moles of component "1" (the heat of combustion $\Delta H_{c,T_0}$ at the temperature T_0 has been measured for it), we have:

$$m_{0,1}\Delta H_{c,T_0} = -\int_{T_0}^{T'} \sum_i m_i C_{p,i}\, dT \tag{4.9}$$

The right-hand side of Eq. (4.9) can be represented as a linear polynomial relative to T' as has been done in the preceding section. From this equation, we find T'.

2. Next we find the heat of the reaction $\Delta H_{c,T'}$ and the equilibrium constant $K_{x,T'}$.

3. We use the value of $K_{x,T'}$ to determine the equilibrium degree of conversion y' of component "1" at the temperature T'.

4. We refine the calculations of the adiabatic combustion temperature by replacing $\Delta H_{c,T_0}$ in formula (4.9) with the mean value ΔH_c:

$$\overline{\Delta H_c} = \frac{\Delta H_{c,T_0} + \Delta H_{c,T'}}{2} \tag{4.10}$$

and $m_{0,}$ and m_i in formula (4.9) with the amounts reacting up to equilibrium at T', namely, $m_1' = m_{0,1}y'$, m_2', ... Now the working formula becomes:

$$m_{0,1}x'\overline{\Delta H_c} = -\int_{T_0}^{T''} \sum_i m_i' C_{p,i}\, dT \tag{4.11}$$

We find the precised temperature T'' of adiabatic combustion from Eq. (4.11).

We next repeat steps 2-4 until one of the iterations yields sufficiently close initial and calculated combustion temperatures.

This method is inferior in its accuracy to the strict approach—solution of the system of equations (4.1)-(4.5). A number of assumptions have also been made in it, for example on the heating of the combustion products. However, the simplicity of the calculations has attracted attention to this method [5, 19].

Let us consider as an example the calculations by the approximate method for the combustion of H_2 in air [80% (mole) N_2, 20% (mole) O_2] with a stoichiometric ratio of the H_2 and O_2. This signifies that the initial mixture contains 0.5 mole of O_2 and 2 moles of N_2 per mole of H_2. Data on the heat of combustion, equilibrium constant, and heat capacities of the components have been given in Sec. 4.3.

1. We estimate the adiabatic temperature of heating the combustion products. With complete combustion, the amounts of the components are as follows (in moles):

Component	N_2	O_2	H_2	H_2O	Total
Beginning of process (in)	2	0.5	1	0	3.5
End of process (out)	2	0	0	1	3

Since

$$C_{p,\text{out}} = 2C_p(N_2) + C_p(H_2O) = 84.96 + 20.04 \times 10^{-3}T \text{ J/K}$$

we have

$$241\,835 = 84.96\,(T' - 298) + \frac{20.04\times10^{-3}}{2}\,[(T')^2 - 298^2]$$

Hence

$$10.02 \times 10^{-3}(T')^2 + 84.96(T') - 268\,042.9 = 0 \text{ and } T' = 2448 \text{ K}$$

A comparison with the data of the preceding example reveals that the use of the "theoretical" (stoichiometric) ratio of hydrogen and oxygen instead of a three-fold excess of oxygen makes it possible to raise the temperature of adiabatic heating by almost 1200 K. At the same time, at 2448 K incomplete oxidation of the hydrogen because of thermodynamic restrictions is possible.

2. We determine $\Delta H_{c,2448}$ and $K_{x,2448}$:

$$\Delta H_{c,2448} = -241\,835 - 11.56\,(2448 - 298) + \frac{3.59\times10^{-3}}{2}\,(2448^2 - 198^2)$$
$$= -256\,064 \text{ J}$$

$$\ln\frac{K_{x,2448}}{K_{x,298}}$$
$$= \int_{298}^{2448} \frac{-241\,835 - 11.56\,(T - 298) + (3.59\times10^{-3}/2)\,(T - 298)^2}{RT^2}\,dT$$
$$= -\left(\frac{241\,835}{8.31} - \frac{11.56\times298}{8.31} + \frac{3.59\times10^{-3}}{2\times8.31}\cdot 298^2\right)\left(\frac{1}{298} - \frac{1}{2448}\right)$$
$$- \frac{11.56}{8.31}\ln\frac{2448}{298} + \frac{3.59\times10^{-3}}{2\times8.31}\,(2448 - 298)$$

whence

$$K_{x,2448} = 10^{-37.8} \times 10^{40} = 158.5$$

3. We determine the equilibrium degree of conversion of hydrogen y at the found value of $K_{x,2448}$. For our example, $m'(H_2) = 1 - y$, $m'(O_2) = 0.5 - 0.5y$, $m'(H_2O) = y$, and $\sum_i m_i = 3.5 - 0.5y$. Therefore

$$158.5 = \frac{y\,(3.5 - 0.5y)^{1/2}}{(1-y)\,(0.5 - 0.5y)^{1/2}} \quad \text{and} \quad y = 0.95$$

4. We find $\overline{\Delta H}_c$:

$$\overline{\Delta H}_c = \frac{-241\,835 - 256\,064}{2} = -248\,950 \text{ J}$$

5. The amounts of the components at the end of the process at $y = 0.95$ are:

$$m'(H_2) = 0.05, \quad m'(O_2) = 0.025, \quad m'(H_2O) = 0.95$$
$$m'(N_2) = 2$$

6. We find the expression of $\sum_i m_i' C_{p,i}$:

$$\sum_i m_i' C_{p,i} = 0.05\,(29.07 - 0.50 \times 10^{-3} T) + 0.025\,(25.70 + 12.98 \times 10^{-3} T)$$
$$+ 0.95\,(30.36 + 9.58 \times 10^{-3} T) + 2\,(27.30 + 5.23 \times 10^{-3} T)$$
$$= 85.53 + 20.16 \times 10^{-3} T \text{ J/K}.$$

7. We determine the precised temperature of adiabatic combustion T'' from the equation

$$0.95 \times 248\,950 = \int_{298}^{T''} (85.53 + 20.16 \times 10^{-3} T)\, dT$$

or

$$2\,36\,502 = 85.53\,(T - 298) + 10.08 \times 10^{-3}\,(T^2 - 298^2)$$

Solution of this quadratic equation yields the value of $T'' = 2400$ K. Since T' and T'' are sufficiently close (they differ by less than 50 K), further refinement of the solution is unnecessary.

Thus, when hydrogen burns in the air with a stoichiometric amount of oxygen, the heating temperature reaches 2400 K; the equilibrium conversion of the hydrogen is 95%.

4.5. Complex Reactions

In real processes, several reactions generally proceed simultaneously.

Of the greatest scientific and practical interest is the studying of the isobaric adiabatic combustion of fuels. Here the burning fuel can consist of several components, or secondary reactions become possible when the combustion products are heated to temperatures exceeding 2000 K, namely, $2CO_2 \rightarrow 2CO + O_2$, $2H_2O \rightarrow 2H_2 + O_2$, $H_2 \rightarrow 2H$, $O_2 \rightarrow 2O$, $H_2O \rightarrow H + OH$, and so on.

Thus, the combustion of hydrogen in air at high temperatures is described by more than 20 reactions.

Consequently, the task arises of calculating complex adiabatic reactions each of which in an isobaric process is characterized by the heat ΔH and the equilibrium constant K_x. The calculations are aimed at determining the temperature of the mixture reached as a result of the complex adiabatic reaction and the amount of components in the mixture. Thus, the calculations of a complex adiabatic reaction differ from those of a complex isothermal one in the need to find the temperature of the equilibrium mixture and in this connection also in the need to take into consideration the effect of the temperature on the heat capacities of the components, and on the heats and equilibrium constants of the reactions.

Initially, as for a complex isothermal reaction, the independent reactions have to be determined. Since in thermodynamic analysis it does not matter whether equilibrium has been reached as a result of p independent or $p_1 > p$ dependent reactions, equilibrium should be considered for p reactions.

This holds both for isothermal and for adiabatic reactions because the heat of a process is determined only by the compositions of the initial and final mixture, but not by how the reactants are converted into the products, i.e. by the number of reactions.

If r components participate in p independent reactions, then as for a complex isothermal reaction, we must express the number of these components in terms of p variables. These are either p "key" (see Sec. 3.1) or p chemical variables, or variables of the universal method (see Sec. 3.5). Assume, for example, that we have selected p key components and written p conditions of equilibrium:

$$\left.\begin{array}{l} K_{x_1} = \prod_1 \left(\dfrac{m_i}{\sum m_i}\right)^{\nu_{i,1}}, \quad K_{x_1} = K_{p_1} p^{-\Sigma\nu_{i,1}} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ K_{x_p} = \prod_p \left(\dfrac{m_i}{\sum m_i}\right)^{\nu_{i,p}}, \quad K_{x_p} = K_{p_p} p^{-\Sigma\nu_{i,p}} \end{array}\right\} \tag{4.12}$$

For each equilibrium constant, we write an equation of an isobar:

$$\left.\begin{array}{l} \dfrac{d \ln K_{p_1}}{dT} = \dfrac{\Delta H_1}{RT^2} \\ \cdots\cdots\cdots \\ \dfrac{d \ln K_{p_p}}{dT} = \dfrac{\Delta H_p}{RT^2} \end{array}\right\} \tag{4.13}$$

For each heat of a reaction, we write the Kirchhoff equation [see formula (4.2)], for example, in the form

$$\left.\begin{array}{l} \Delta H_1 = B_1 + \Delta a_1 T + \Delta b_1 T^2 + \Delta c_1 T^3 \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ \Delta H_p = B_p + \Delta a_p T + \Delta b_p T^2 + \Delta c_p T^3 \end{array}\right\} \tag{4.14}$$

The coefficients B, Δa, Δb, and Δc are found from tabulated data on the temperature dependence of the heat capacity of each of the components (not only the key ones):

$$C_{p,i} = a_i + b_i T + c_i T^2 \tag{4.15}$$

If the component i_k participates only in one i-th reaction and the heat of this reaction ΔH_i has been related to one mole of this component, the total absorption of heat when the amount of each component changes by dm_{ik} is $\sum \Delta H_i \, dm_{ik}$. This heat absorption "removes" the amount of heat $-\sum m_i C_{p,i} \, dT$, and the equation of the heat balance has the form

$$\sum \Delta H_i \, dm_{i,k} = -\sum m_i C_{p,i} \, dT$$

or

$$\sum \Delta H_i \frac{dm_{i,k}}{dT} = -\sum m_i C_{p,i} \tag{4.16}$$

The solution of the system of equations (4.12)-(4.16) enables one to calculate the results of a complex adiabatic reaction, i.e. $m_1, \ldots, m_p$, T. In the general case, a solution is possible using numerical methods and a computer. In specific calculations, the same simplifications are resorted to as for a simple reaction; they have been treated on previous pages.

For illustration, let us consider the compilation of equations for calculating the adiabatic isobaric combustion of methane:

$$CH_4 + 2O_2 \xrightarrow{K_{x_1}} CO_2 + 2H_2O$$

when the dissociation of the CO_2 has to be taken into account:

$$CO_2 \xrightarrow{K_{x_2}} CO + \frac{1}{2} O_2$$

Let the initial mixture contain 3.6 moles of O_2 (an excess factor of 1.2) and $3.6 \times 3.76 = 13.5$ moles of N_2 (3.76 is the volume ratio of N_2 and O_2) per mole of methane.

Both reactions are mutually independent—CH_4 participates only in the first one, and CO only in the second. We choose CH_4 and CO as the key components and express the amounts of the other components, namely, $m(O_2)$, $m(CO_2)$, and $m(H_2O)$ in terms of their number of moles in an equilibrium mixture $m(CH_4)$ and $m(CO)$.

As indicated above, the initial mixture contains one mole of CH_4, 3.6 moles of O_2, and 13.5 moles of N_2.

From the condition of the constancy of the number of atoms of each element, we have:

for C atoms:

$$1 = m(CH_4) + m(CO_2) + m(CO)$$

for H atoms:

$$4 = 4m(CH_4) + 2m(H_2O)$$

for O atoms:

$$7.2 = 2m(O_2) + 2m(CO_2) + m(H_2O) + m(CO)$$

Consequently,

$$m(CO_2) = 1 - m(CH_4) - m(CO)$$
$$m(H_2O) = 2 - 2m(CH_4)$$

$$m(O_2) = 3.6 - m(CO_2) - \frac{1}{2}m(H_2O) - \frac{1}{2}m(CO)$$
$$= 1.6 + 2m(CH_4) + \frac{1}{2}m(CO)$$

$$\sum m_i = m(CH_4) + m(O_2) + m(CO_2) + m(H_2O) + m(CO) + m(N_2)$$
$$= 18.1 + \frac{1}{2}m(CO)$$

Having in view that $x_i = m_i/\sum m_i$ and writing equations (4.12), we obtain:

$$K_{x_1} = K_{p_1}p = \frac{x(CO_2)x^2(H_2O)}{x(CH_4)x^3(O_2)} = \frac{m(CO_2)m^2(H_2O)\sum m_i}{m(CH_4)m^3(O_2)}$$
$$= \frac{[1 - m(CH_4) - m(CO)]\,[2 - 2m(CH_4)]^2\left[18.1 + \frac{1}{2}m(CO)\right]}{m(CH_4)\left[1.6 + 2m(CH_4) + \frac{1}{2}m(CO)\right]^3}$$

$$K_{x_2} = K_{p_2}p^{-\frac{1}{2}} = \frac{x(CO)x^{\frac{1}{2}}(O_2)}{x(CO_2)} = \frac{m(CO)m^{\frac{1}{2}}(O_2)}{m(CO_2)\left(\sum m_i\right)^{\frac{1}{2}}}$$
$$= \frac{m(CO)\left[1.6 + 2m(CH_4) + \frac{1}{2}m(CO)\right]^{\frac{1}{2}}}{[1 - m(CH_4) - m(CO)]\left[18.1 + \frac{1}{2}m(CO)\right]^{\frac{1}{2}}}$$

Let the reaction heats ΔH_1 and ΔH_2 be calculated per mole of CH_4 and CO, respectively. Their temperature dependence is given in the form of Eq. (4.14). It is not difficult to write the equations of an isobar (4.13) and equations (4.15) for the heat capacities of all the components—six equations.

The heat balance equation will be as follows:

$$\Delta H_1 \frac{dm(CH_4)}{dT} + \Delta H_2 \frac{dm(CO)}{dT} = -[m(CH_4)C_p(CH_4) + m(O_2)C_p(O_2) + m(CO_2)C_p(CO_2) + m(H_2O)C_p(H_2O) + m(CO)C_p(CO) + m(N_2)C_p(N_2)]$$

Thus, performing of the calculations requires the solution of a system of 11 equations, which is possible only with the use of search techniques and numerical calculations using a computer. Approximate solutions can also be used. The approximations are the same as for simple reactions (see Secs. 4.3 and 4.4). Examples of the results of calculating complex adiabatic reactions are given in [5, 7].

Table 9. **Content of Components in the Products of Combustion of Hydrocarbons in Oxygen at a Pressure of 1 MPa**

Temperature, K	Content of components in equilibrium mixture, mole fractions							
	H_2O	CO_2	CO	H_2	O_2	H	O	OH
2000	0.42	0.35	0.18	0.05	—	—	—	—
3000	0.39	0.28	0.23	0.06	0.02		0.02	
4000	0.10	0.05	0.33	0.06	0.05	0.13	0.11	0.17
6000	—	—	0.22	—	—	0.40	0.35	0.03

Table 9 gives the composition of an equilibrium mixture of the combustion products of hydrocarbons in oxygen at various temperatures and a pressure of 1 MPa [20].

Table 10. **Adiabatic Temperature of Combustion**

Oxidizing agent	Fuel	Oxidizing agent excess factor	Pressure, MPa	T_{ad}, K
Air	Hydrogen	1	0.1	2400
Air	Acetylene	1	0.1	2500
Air	Hydrocarbon (octane)	1	0.1	2300
Air	Kerosene	1	0.1	2400
Air	Ditto	2	1.0	1500
Air	Ditto	3	1.0	1200
Air	Ditto	4	1.0	900
Oxygen	Hydrogen	1	0.1	3100
Oxygen	Kerosene	1	7.0	3700
Oxygen	Pentaborane	1	7.0	4500
Fluorine	Hydrazine	1	4.0	4500
Fluorine	Hydrogen	0.5	2.8	4700
Nitric acid	Kerosene	0.9	4.0	3100

Examination of Table 9 reveals that the exact calculations of the adiabatic combustion temperature require that account be taken of the dissociation of molecules into atoms and radicals only at temperatures above 3000 K. Table 10 presents calculated data on the adiabatic combustion temperature T_{ad} [20].

Chapter 5

Heats of Industrial Hydrocarbon Treatment Processes

5.1. Petroleum Fraction Treatment Processes

By using standard thermodynamic tables, one can easily calculate the heat of a simple reaction with the participation of individual substances. In industrial processes of petroleum fraction treatment, a large number of substances react and participate in a still larger number of simple reactions. Consequently, the heats of industrial processes can be determined and calculated by the following methods.

1. Experimental determination of the heat of a process when it is conducted in an adiabatic reactor from measurements of the temperature increment $\Delta T_{ad} = T_{out} - T_{in}$. Assume that G_0 kg/h of feed stock and G_d kg/h of a diluent are fed into a reactor, the heat capacity of the reacting mixture being C_p kJ/(kg·K). Hence, the heat of the process q_{pr} (in kJ/kg of raw material) is:

$$q_{pr} = -\frac{G_0+G_d}{G_0} C_p \Delta T_{ad} \tag{5.1}$$

This method is sufficiently simple, but the running of experiments within a broad range of temperatures for various kinds of feed stock and at various degrees of conversion requires a long time. Moreover, one must be sure that the heat losses through the walls in a real reactor are insignificant and that the conditions are indeed close to adiabatic ones. This is why experimental investigations are used only for random checking of the accuracy of the calculation methods.

2. The exact experimental determination of the material balance of a process and the heats of combustion ΔH_c of unit masses of the reactants and products. If the masses g_{A_1} and g_{A_2} of the reactants have been used up and the masses $g_{A_1'}$ and $g_{A_2'}$ of the products have been obtained, the heat of such a process is

$$q_{pr} = (g_{A_1}\Delta H_{c,A_1} + g_{A_2}\Delta H_{c,A_2}) - (q_{A_1'}\Delta H_{c,A_1'} + q_{A_2'}\Delta H_{c,A_2'})$$

Table 11 and Fig. 12 present data on the heats of combustion of petroleum products with the formation of water vapour (the lower heat) and liquid water (the higher heat) that are customarily used in heat calculations. The density and chemical composition of petroleum products may differ substantially from the values given in Table 11. The values of ΔH_c will differ accordingly. It is therefore good in each specific case to use the working relations given herein.

Table 11. **Heats of Combustion of Petroleum Products**

Product	Density, g/cm³	Content, mass %					Heat of combustion $-\Delta H_c$, kJ/kg	
		water	C	H	S	Ash	higher*	lower**
Butane	0.581	—	83.0	17.0	—	—	50 795	47 195
Petrol	0.716	—	86.0	14.0	—	—	47 445	44 185
Fuel oil (mazut)	0.923	0.05	87.4	11.1	0.42	1.03	43 644	31 210
Thermal cracking residue	0.991	0.3	86.5	10.0	1.5	1.7	42 050	39 830
Tar	1.014	0.25	88.5	9.1	0.7	1.5	42 000	41 650
Bunker fuel	1.017	0.10	87.5	9.4	1.4	1.6	41 760	39 710
Petroleum coke	—	1.2	96.0	2.1	0.4	0.3	35 440	34 980

* To liquid water.
** To water vapour.

The heats of combustion (in kJ/kg) of the liquid fractions (to liquid water) are calculated with the aid of formulas in which ΔH_c is related to the elemental composition of the feed stock [the content in the feed stock (in mass fractions) of carbon—z_C, hydrogen—z_H, sulphur—z_S, oxygen—z_O, and moisture—z_{H_2O}]:

$$-\Delta H_c = 340z_C + 1029z_H + 109(z_S - z_O) - 257z_{H_2O} \quad (5.2)$$

or to the density ρ at 15 °C (in g/cm³):

$$-\Delta H_c = 51\,882 - 8786\rho^2 \quad (5.3)$$

For example, in the delayed coking of tar ($\rho = 0.975$ g/cm³), there was obtained 6.2% of gas, 12.1% of petrol ($\rho = 0.74$ g/cm³), 39.4% of light gas oil ($\rho = 0.86$ g/cm³), 22.7% of heavy gas oil ($\rho = 0.91$ g/cm³), and 19.6% of coke. Let us find the heat of the process from the heats of combustion of the feed stock and the products. Using Eq. (5.3) relating ΔH_c and the density for the liquid products, and also tabulated data on the heats of combustion of gas and coke, we obtain:

Substance	Tar	Gas	Petrol	Light gas oil	Heavy gas oil	Coke
Heat of combustion ΔH_c, kJ/kg	—43 515	—53 000	—47 100	—44 850	—44 430	—35 440

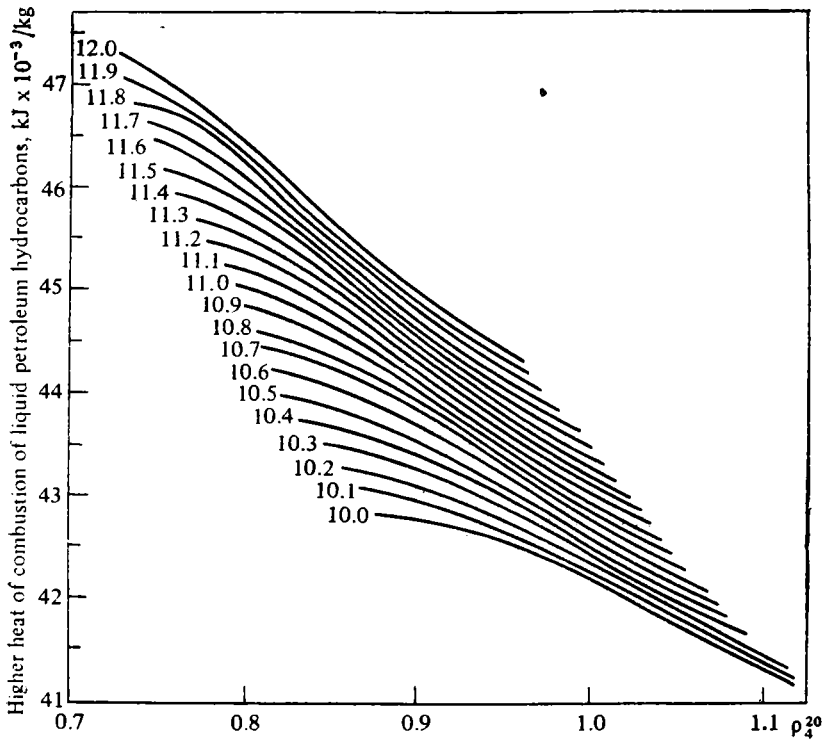


Fig. 12. Graph for determining the heat of combustion of liquid petroleum hydrocarbon fractions to liquid water (the higher heat of combustion).

ρ_4^{20} is the ratio of the density of a petroleum product at 20 °C to that of water at 4 °C; the numbers on the curves are the characterizing factor $K = 1.216\sqrt{t + 273}/\rho_4^{20}$, where t is the mean boiling point of the fraction, °C

The heat of the process is

$$q_{pr} = -43\,515 + (0.062 \times 53\,000 + 0.121 \times 47\,100 + 0.394 \times 44\,850 + 0.227 \times 44\,430 + 0.196 \times 35\,440) = 173 \text{ kJ/kg}$$

Notwithstanding its apparent simplicity, this method is employed rarely because it requires very accurate measurements. Indeed, the heats of hydrocarbon treatment processes rarely exceed 400 kJ/kg, whereas the heats of combustion have values from 30 000 to 60 000 kJ/kg, i.e. a relative error in determining the heat of combustion of a product of 1% can lead to an error of 100% and more in calculating the heat of a technical process. The empirical relations for calculating the heats of combustion of hydrocarbon mixtures yield a relative error of at least 2%, and, consequently, they cannot be employed. It should also be noted that the given method is not

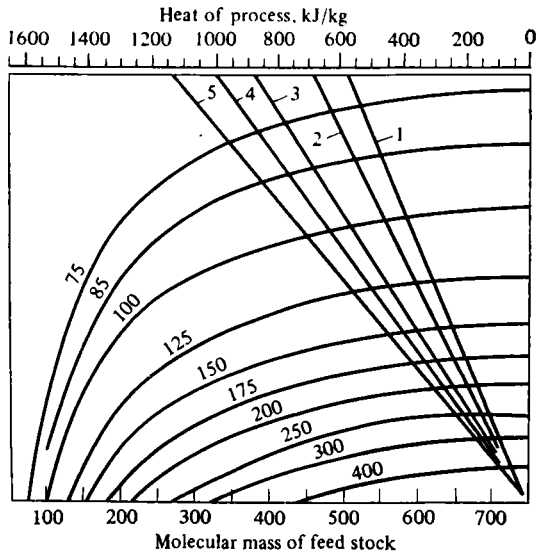


Fig. 13. Data on the heats of industrial petroleum treatment processes:
1 – hydrogenation of polymer petrol; *2* – hydrofining of gas oil; *3* – platforming; *4* – catalytic cracking of light gas oil; *5* – catalytic cracking of heavy gas oil. The numbers on the curves are the molecular mass of the products

convenient if one desires to obtain a working relation for the heat of a technical process.

The methods of calculation treated above do not allow one to establish with sufficient reliability the true heats of industrial processes or even the possible regions of their change owing to the inaccuracy in determining the conditional enthalpies of the petroleum fractions or their heats of combustion. One therefore has to compare a calculated value with one previously published in the literature to assess its authenticity. Thus, Figs. 13 and 14 present data on the heats of industrial processes of petroleum treatment collected by Gurevich [21] by analysing industrial data and on the basis of calculations using the conditional enthalpies. Although the order of magnitude of the quantities and their sign have been established correctly, the discrepancies between the data of different authors is substantial. Thus, from the data of Fig. 13, the heat of the catalytic cracking of gas oil can reach almost 1000 kJ/kg, whereas from the data of Fig. 14 it is only about 300 kJ/kg.

The method of calculations considered below is the most accurate one. It enables one to perform heat calculations of processes with complex mixtures on the basis of the exactly established heats of reactions of individual hydrocarbons.

3. If the scheme of a process has been determined and group components such as alkanes C_nH_{2n+2} are considered as the reactants, we can take advantage of the molar heat of a simple process being independent of the molecular mass of the feed stock. The heat of a complex process can be found as the sum of the heats of the individual steps. It is usually convenient for this purpose to consider the equations of the material and heat balances together.

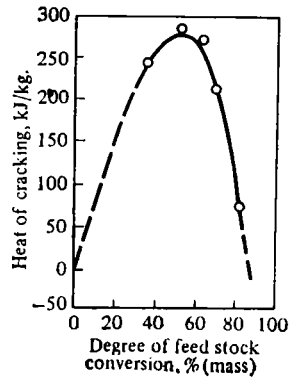


Fig. 14. Heat of cracking versus the degree of conversion of the feed stock

We used this approach in our investigations for calculating the heats of large-scale petroleum refining processes [8, 22]. We shall show below how this approach was used to find the heats of processes of catalytic cracking, platforming, hydrocracking—hydrofining, and so on. We use the thermodynamic characteristics of simple reactions for individual model substances representing the reactants and products, and also the equations of the material and heat balances. The type of reactor used is of no significance when finding the heat of a process. It is only important whether a process is carried on under isobaric or isochoric conditions because ΔH and ΔU are different for reactions in a gas phase. Since, however, the conditions of flow in industrial reactors are close to ideal displacement, below we shall use the equations of the balances for ideal-displacement reactors. The mathematical descriptions are also used for mathematical modelling [8].

When writing the equations of the balances of petroleum fraction treatment processes, the reactants are combined either according to technological features (gas, petrol, diesel fuel, etc.) or to their chemical features (alkanes, cycloalkanes, etc.). Accordingly, we speak of technological or chemical grouping. The latter is more convenient for heat calculations because it allows us to use accurate data on the heats of reactions of individual hydrocarbons and their derivatives.

An analysis of data on the heats of reactions of individual hydrocarbons has shown that the heat of a reaction for stoichiometric amounts of the reactants does not virtually depend on the molecular mass of the initial substance. For example, the heats of cracking of *n*-hexane, *n*-heptane, and *n*-octane with the formation of ethylene and an alkane are close in value, as are the heats of isomerization of various hydrocarbons, and so on. The heats of reactions of individual hydrocarbons are compared in Table 12.

Table 12. **Heats of Various Transformations of Individual Hydrocarbons**

Reaction	Heat of reaction ΔH° (kJ/mol) at temperatures, K		
	700	800	900
Cracking of normal alkanes (into *n*-alkane and ethylene):			
$n\text{-}C_6H_{14} \rightarrow C_2H_4 + n\text{-}C_4H_{10}$	91.1	90.3	89.5
$n\text{-}C_8H_{18} \rightarrow C_2H_4 + n\text{-}C_6H_{14}$	91.1	90.7	89.9
$n\text{-}C_{10}H_{22} \rightarrow C_2H_4 + n\text{-}C_8H_{18}$	91.1	90.3	89.9
$n\text{-}C_{12}H_{26} \rightarrow C_2H_4 + n\text{-}C_{10}H_{22}$	91.1	90.3	89.9
(into *n*-alkane and *n*-alkene C_3-C_5):			
$n\text{-}C_{12}H_{26} \rightarrow C_3H_6 + n\text{-}C_9H_{20}$	78.6	77.7	76.5
$n\text{-}C_{12}H_{26} \rightarrow n\text{-}C_4H_8 + n\text{-}C_8H_{18}$	79.0	77.7	76.9
$n\text{-}C_{12}H_{26} \rightarrow n\text{-}C_5H_{10} + n\text{-}C_7H_{10}$	79.0	77.7	76.9
Isomerization of normal alkanes:			
$n\text{-}C_6H_{14} \rightarrow iso\text{-}C_6H_{14}$	—6.3	—5.9	—5.9
$n\text{-}C_8H_{18} \rightarrow iso\text{-}C_8H_{18}$	—4.2	—4.2	—4.2
Isomerization of six-membered cycloalkanes (into five-membered cycloalkanes):			
$C_6H_{12} \rightarrow C_5H_9 - CH_3$	15.5	14.2	13.4
$C_6H_{11}CH_3 \rightarrow C_5H_8(CH_3)_2$	16.7	15.5	14.2
Dehydrocyclization of alkanes (with formation of cycloalkanes):			
$n\text{-}C_6H_{14} \xrightarrow[-H_2]{} C_6H_{12}$	45.1	46.4	47.7
$n\text{-}C_8H_{18} \xrightarrow[-H_2]{} C_6H_{11} - C_2H_5$	40.5	42.6	44.3
$n\text{-}C_{10}H_{22} \xrightarrow[-H_2]{} C_6H_{11} - n\text{-}C_4H_{10}$	41.4	43.1	44.7
$n\text{-}C_{12}H_{26} \xrightarrow[-H_2]{} C_6H_{11} - n\text{-}C_6H_{13}$	41.4	43.1	45.1
Dehydrogenation of six-membered cycloalkanes (into aromatics):			
$C_6H_{12} \xrightarrow[-3H_2]{} C_6H_6$	219.9	220.9	219.9
$C_6H_{11} - C_2H_5 \xrightarrow[-3H_2]{} C_6H_5 - C_2H_5$	212.8	212.8	211.5
$C_6H_{11} - C_4H_9 \xrightarrow[-3H_2]{} C_6H_5 - C_4H_9$	209.8	209.8	209.0
Hydrocracking of alkanes (with the formation of methane and *n*-alkane):			
$n\text{-}C_6H_{14} \xrightarrow{+H_2} CH_4 + n\text{-}C_5H_{12}$	—60.6	—61.9	—63.5
$n\text{-}C_8H_{18} \xrightarrow{+H_2} CH_4 + n\text{-}C_7H_{16}$	—60.6	—61.9	—63.5
$n\text{-}C_{10}H_{22} \xrightarrow{+H_2} CH_4 + n\text{-}C_9H_{20}$	—60.6	—61.9	—63.5

Table 12 (*concluded*)

Reaction	Heat of reaction $\Delta H°$ (kJ/mol) at temperatures, K		
	700	800	900
(with the formation of *n*-alkanes C_2 and higher):			
$n\text{-}C_{10}H_{22} \xrightarrow{+H_2} C_2H_6 + n\text{-}C_8H_{18}$	—51.4	—52.7	—54.3
$n\text{-}C_{10}H_{22} \xrightarrow{+H_2} C_3H_8 + n\text{-}C_7H_{16}$	—49.7	—51.0	—52.7
$n\text{-}C_{10}H_{22} \xrightarrow{+H_2} n\text{-}C_4H_{10} + n\text{-}C_6H_{14}$	—51.4	—52.7	—53.9
Dehydrogenation of alkanes (into alkenes):			
$n\text{-}C_6H_{14} \xrightarrow[-H_2]{} n\text{-}C_6H_{12}$	130.0	130.4	129.2
$n\text{-}C_8H_{18} \xrightarrow[-H_2]{} n\text{-}C_8H_{16}$	125.8	127.5	129.2
$n\text{-}C_{10}H_{22} \xrightarrow[-H_2]{} n\text{-}C_{10}H_{20}$	125.8	130.4	130.4

It is more convenient to use the molar heats of reactions of individual substances as the initial ones in calculations of heats. An analysis of Table 12 also shows that within the temperature interval of 700-900 K, i.e. for most industrial processes, the heats of reactions depend only slightly on the temperature. In general, the change in the temperature in a process by 100-200 K hardly affects the heat of the reaction. This is why in the thermal calculations of real non-isothermal processes one may disregard the effect of the temperature on the reaction heat.

If data on the change in the chemical components during a process are absent, but the amounts of obtained technical fractions are known, technological grouping is employed. Here certain difficulties arise with the use of data on the heats of reactions of individual substances. For example, the cracking of gas oil can be considered by using data on the cracking of an *n*-alkane of the same molecular mass as the mean molecular mass of the fraction, but data can also be used on the heat of cracking of alkylbenzene, and so on. Hence, the use of a technological grouping for heat calculations requires the verification of the derived relations on the basis of the experimentally measured heats of the relevant processes.

The approach treated below is a considerably more accurate one than those described above. It enables one to obtain reliable calculated data on the heats of industrial processes.

5.1.1. Gas Oil Fraction Catalytic Cracking

Use of a Technological Grouping. If cracking is treated as a single-step process "feed stock → products", the following equations of the material and heat balances (for an elementary volume of the reactor) will be a mathematical description of a process in an adiabatic ideal-displacement reactor:

$$-\frac{dG_A}{dv}=w, \quad -\frac{dT}{dv}=\frac{1}{G_AC_A+G_{cat}C_{cat}}q_{pr}w$$

where G_A and C_A are the rate of flow and the heat capacity of the feed stock, respectively, G_{cat} and C_{cat} are the same for the catalyst, T is the temperature, w is the rate of cracking measured in kilogrammes of converted feed stock per unit time per unit reactor volume, and q_{pr} is the heat of cracking related to one kilogramme of the converted feed stock.

By considering q_{pr}, G_AC_A and $G_{cat}C_{cat}$ to be constant and integrating the equation of the heat balance (for which purpose we substitute $-dG_A/dv$ for w in it), we obtain:

$$\int_{T_0}^{T} dT=\frac{1}{G_AC_A+G_{cat}C_{cat}}q_{pr}\int_{G_A}^{0} dG_A$$

whence

$$q_{pr}=\frac{G_AC_A+G_{cat}C_{cat}}{G_A}(T_0-T) \tag{5.4}$$

Table 13 presents the heats of reactions calculated by Eq. (5.4) in accordance with data of operating an industrial installation.

For example, let us use the data of Table 13 to calculate the heat of catalytic cracking of feed stock with a boiling point of 233-350 °C, having in view that the heat capacity of the feed stock is $C_A = 2.93$ kJ/(kg·K) and that of the catalyst is $C_{cat} = 1.04$ kJ/(kg·K), using Eq. (5.4):

$$q_{pr}=\frac{48.4\times2.93+99.6\times1.04}{48.4}(497-454)=218.0 \text{ kJ/kg}$$

This value is given in Table 13.

The heat of catalytic cracking under industrial conditions (approximately 150-250 kJ/kg) agrees well with calculated values. The cited heats relate to one kilogramme of fuel fed into a reactor. When the degree of conversion of the feed stock increases, the heat should grow, which is confirmed by the data of the industrial installation. Thus, when the conditional degree of conversion of the feed stock (i.e. the sum of the yields of petrol, gas, and coke) increases from 63 to 80.7%, the heat of the process grows from 180 to 202 kJ/kg.

It should be noted that the change in the heat of a reaction with a change in the extent of the relevant process points to a simplified

Table 13. **Heats of Catalytic Cracking Determined from Data on the Operation of an Industrial Installation**

Item	Intervals of feed stock boiling, °C				
	233-350	258-332	239-350	240-350	242-350
Mass flow of feed stock, tonne/h	48.4	46.4	45.7	48.3	45.4
Ditto, catalyst, tonne/h	99.6	95.8	99.1	99.1	95.6
Conditional degree of conversion of feed stock, mass %	100	76.5	100	63.1	80.7
Equilibrium temperature at reactor top, °C	497	485	492	483	492
Temperature at reactor outlet, °C	454	448	452	452	452
Heat of process, kJ/kg	218	185	204	180	202

selection of the scheme. Indeed, more involved schemes, for example, a two-step one, are used to describe catalytic cracking [8, 13]:

$$A \xrightarrow{w_1} \nu_{11}A_g + \nu_{21}A_{lr} + \nu_{31}A_{hr} + \nu_{41}A_c$$

$$A_{lr} \xrightarrow{w_2} \nu_{12}A_g + \nu_{22}A_{hr} + \nu_{32}A_c$$

where A is the feed stock, A_g is the gas, A_{lr} is the light reflux (petrol + diesel fuel), A_{hr} is the heavy reflux, A_c is the coke, ν_{ij} is the yield of the i-th product in the complete decomposition of the initial substance, and w_1 and w_2 are the rates of the process

We obtain a mathematical description of a two-step process in an adiabatic ideal-displacement reactor in the form of three equations (material balances for A and A_{lr} and a heat balance); all the equations are written for an elementary volume dv of the reactor:

$$-\frac{dG_A}{dv} = w_1, \quad \frac{dG_{lr}}{dv} = \nu_{21}w_1 - w_2$$

$$-\frac{dT}{dv} = \frac{1}{G_A C_A + G_{cat} C_{cat}} (q_1 w_1 + q_2 w_2)$$

where q_1 and q_2 are the heats of the steps.

Substituting for w_1 and w_2 in the third equation their values from the first two, we obtain an equation in total differentials. Its integration yields:

$$T_0 - T = (q_1 - \nu_{21}q_2)\frac{G_A}{G_A C_A + G_{cat} C_{cat}} + q_2 \frac{G_{lr}}{G_A C_A + G_{cat} C_{cat}} \quad (5.5)$$

where G_{lr} is the rate of flow of the light reflux (A_{lr}) at the reactor outlet; the remaining symbols are the same as above.

Having data on the material and heat balances, we can find q_1 and q_2 by Eq. (5.5), using the method of least squares. For reliable determination of q_1 and q_2, data are needed on several regimes of treatment of feed stock of a single kind. Experimental data on the operation of a catalytic cracking reactor are given in [13]. They yielded the values of $q_1 = 272$ kJ/kg and $q_2 = -66$ kJ/kg, i.e. both endothermic ($q > 0$) and exothermic ($q < 0$) reactions proceed in cracking.

Use of a Chemical Grouping. We can propose working relations for the heat of catalytic cracking by using the notions on the transformations of group components. In cracking, decomposition occurs along the C—C bonds (in alkanes, a cycloalkane ring, an alkyl group with an aromatic or cycloalkane nucleus), the decomposition being attended by the redistribution of the hydrogen. Assume that for an alkane feed stock, the reaction with redistribution of the hydrogen has the form

$$C_nH_{2n+2} \rightarrow \nu_{alk}C_{n_1}H_{2n_1+2} + \nu_{ol}C_{n_1}H_{2n_1} + C_{n-(\nu_{alk}+\nu_{ol})n_1}H_{2[n+1-\nu_{alk}-(\nu_{alk}+\nu_{ol})n_1]}$$

where ν_{alk} is the amount (1 mole per mole of feed stock) of alkanes formed in cracking with the average number n_1 of carbon atoms for the low-boiling product, and ν_{ol} is the same for the low-boiling alkenes (olefins).

The last compound on the right-hand side characterizes heavy fractions enriched with carbon. If $n - (\nu_{alk} + \nu_{ol})n_1 = 0$, these products do not form; when this quantity is greater than zero, they must be taken into account, while when $n - (\nu_{alk} + \nu_{ol})n_1 < 1$, the products contain more hydrogen than the feed stock does. In this case, the hydrogen is obviously introduced into the system, as, for example, in the hydrocracking process treated below.

In the cracking of a technical feed stock, the investigator has at his disposal data on the molecular mass M of the stock and M_i of the products, and the mass yields of the products Y_i. Using these data, we can easily determine the average number n of carbon atoms in the feed stock and n_i of these atoms in the products:

$$n = \frac{M-2}{14}, \quad n_i = \frac{M_i-2}{14}$$

Here 14 is the molecular mass of the CH_2 group.

We can also use the expression

$$n = \frac{1}{14}\left(\frac{1}{\sum Y_i/M_i} - 2\right) \tag{5.6}$$

In cracking, the heat q_{pr} of a process depends only on the ratio of the normal and isostructures of the alkenes (olefins) and alkanes; the

value of q_{pr} is not affected appreciably by n and the temperature of the process.

It is general knowledge that isoalkanes and n-alkenes predominate in the products of catalytic cracking [23]. Thus, in cracking on zeolites, the ratio of the normal and isoalkanes $\alpha_{alk}^{n/iso} = 1/\alpha_{alk}^{iso/n}$ ranges from 0.15 to 0.20; for an amorphous aluminosilicate catalyst it is 0.15. The ratios of the normal and isoalkenes $\alpha_{ol}^{n/iso} = 1/\alpha_{ol}^{iso/n}$ for the above catalysts are 12-15 and 32, respectively. If we assume that $\alpha^{iso/n} = 25$ characterizes isostructures, and $\alpha^{iso/n} = 0$—normal hydrocarbons, then processing of the above data yields:

$$q = 78.5 - 0.16\alpha_{alk}^{iso/n} - 0.68\alpha_{ol}^{iso/n} \qquad (5.7)$$

$$\text{(for isostructures, } \alpha_{alk}^{iso/n} = \alpha_{ol}^{iso/n} = 25)$$

Table 14 presents data on the influence of the alkene:alkane ratio in cracking products by the obtained equation, i.e. of the quantity ν_{ol}/ν_{alk}, on the heat q_{pr} of a process. Data on the heats of formation

Table 14. **Heats of Cracking of n-Dodecane with the Formation of Various Amounts of an Alkene, Alkane, and Heavy Fractions***

Reaction	ν_{ol}/ν_{alk}	Heat q_{pr} (kJ/mol) at temperatures, K	
		800	900
$n\text{-}C_{12}H_{26} \rightarrow n\text{-}C_6H_{12} + n\text{-}C_6H_{14}$	1	79	78
$n\text{-}C_{12}H_{26} \rightarrow 0.6n\text{-}C_6H_{12} + 1.2n\text{-}C_6H_{14} + C_{1.2}H_2$	0.5	78	77
$n\text{-}C_{12}H_{26} \rightarrow 0.4n\text{-}C_6H_{12} + 1.4n\text{-}C_6H_{14} + C_{1.2}H_{1.2}$	0.29	52	51
$n\text{-}C_{12}H_{26} \rightarrow 0.2n\text{-}C_6H_{12} + 1.6n\text{-}C_6H_{14} + C_{1.2}H_{1.2}$	0.125	25.5	25
$n\text{-}C_{12}H_{26} \rightarrow 0.1n\text{-}C_6H_{12} + 1.7n\text{-}C_6H_{14} + C_{1.2}H$	0.06	13	12

* $C_{1.2}H_2$, $C_{1.2}H_{1.2}$, and $C_{1.2}H$ are the chemical composition of the heavy fractions formed from one mole of feed stock.

of the individual substances have been used in the calculations; the heavy fractions are polycyclic aromatic hydrocarbons; the heat of formation related to one mole of carbon atoms for them can be considered constant and equal to about 10 kJ/mol.

The data of Table 14 can be approximated by a polynomial giving the dependence of q on ν_{ol}/ν_{alk} with an arbitrary value of the latter

ratio:

$$\frac{q_{ol/alk}}{q_{ol/alk=0.5-1}} = \begin{cases} 0.018 + 2.55(\nu_{ol}/\nu_{alk}) - 1.08(\nu_{ol}/\nu_{alk})^2 & \text{at } \nu_{ol}/\nu_{alk} < 0.5 \\ 1 & \text{at } \nu_{ol}/\nu_{alk} = 0.5\text{-}1 \end{cases} \tag{5.8}$$

The error of the calculations does not exceed 2 kJ/mol.

Calculations by Eqs. (5.7) and (5.8) enable us to determine the heat of a reaction with the formation of two "large" fragments with the breaking of one C—C bond. But in real processes, the number r of bonds being broken per molecule of the feed stock can also be greater than unity, and the heat of the process $q_{pr} = rq$, where q has been determined above and characterizes the breaking of one C—C bond. The value of r can be found from the difference between the numbers of bonds in the feed stock $(n - 1)$ and in the products $\sum \nu_i (n_i - 1)$ with a lower boiling point than that of the feed stock:

$$r = (n-1) - \sum \nu_i (n_i - 1) = \frac{M-16}{14} - \sum \nu_i \frac{M_i - 16}{14} \tag{5.9}$$

Here ν_i is the number of moles of the i-th lower-boiling fraction formed when the feed stock decomposes completely.

If Y_i is the yield of the i-th fraction, and Y is the yield of the fraction coinciding in its boiling point with that of the feed stock, we have:

$$\nu_i = \frac{Y_i M}{(1-Y) M_i} \tag{5.10}$$

We can assume for simplification that $1 - Y \approx \sum Y_i$.

Introducing Eqs. (5.9) and (5.7) into the equation $q_{pr} = rq$ with a view to Eq. (5.10), we obtain the heat of catalytic cracking related to one kilogramme of feed stock (in kJ/kg):

$$q_{pr} = \frac{1000}{M} \left[\frac{M-16}{14} - \sum \frac{Y_i M}{(1-Y) M_i} \frac{M_i - 16}{14} \right] \times (78.5 - 0.16\alpha_{alk}^{iso/n} - 0.68\alpha_{ol}^{iso/n}) \frac{q_{ol/alk}}{q_{ol/alk=0.5-1}} \tag{5.11}$$

where the ratio $q_{ol/alk}/q_{ol/alk=0.5-1}$ is given by Eq. (5.8), and $1000/M$ is a conversion factor (from moles to kilogrammes).

In the cracking of technical feed stock, the C—C bonds are broken in various groups of hydrocarbons. For complex feed stocks, we can also derive a relation for calculating q_{pr} from a known group composition. In the majority of cases, however, especially for the heavy feed stock of catalytic cracking, the group composition is unknown, and a relation using it becomes meaningless. It should be noted that

no matter what the cracking feed stock is, a change in the ratio of the alkenes (olefins) and alkanes or of the normal and isohydrocarbons in the products affects the heat of the reaction in accordance with Eq. (5.11). It is therefore good to employ it for a feed stock of any composition to take into account the changes in the heat of the process due to the change in the amount and quality of the products because of the use of a different catalyst or regime. The arbitrary composition of the feed stock only leads to the fact that the quantity 78.5 characterizing the decomposition of alkanes must be replaced with an experimentally determined effective quantity X so that (in kJ/kg):

$$q_{pr} = 71.5\left[\frac{M-16}{M} - \sum \frac{Y_i(M_i-16)}{(1-Y)M_i}\right](X - 0.16\alpha_{alk}^{iso/n} - 0.68\alpha_{ol}^{iso/n}) \times \left[0.018 + 2.55\frac{\nu_{ol}}{\nu_{alk}} - 1.08\left(\frac{\nu_{ol}}{\nu_{alk}}\right)^2\right] \quad (5.12)$$

If one has measured the heat of a process at known values of M, Y, M_i, Y_i, $\alpha_{alk}^{iso/n}$, $\alpha_{ol}^{iso/n}$, and ν_{ol}/ν_{alk}, it will not be difficult to find X and q_{pr} by Eq. (5.12).

For illustration, we shall give the results of using Eq. (5.12) to process data on the material balances of the catalytic cracking of technical feed stock with various molecular masses M [24] (see Table 15).

Table 15. **Data on the Catalytic Cracking of Technical Feed Stock**

Item*	Values for molecular mass M equal to		
	198	210	372
Yield, mass fractions:			
gas, Y_1	0.047	0.114	0.095
petrol, Y_2	0.311	0.462	0.370
diesel fuel, Y_3	0.416	0.381	0.280
residue, Y_4	0.108	—	0.230
Ratio, isostructure/normal:			
in alkanes, $\alpha_{alk}^{iso/n}$	1	5.6	5.6
in alkenes (olefins), $\alpha_{ol}^{iso/n}$	1	0	0
Heat of process, kJ/kg:			
as function of X	$1.5(X-0.9)$	$3.6(X-1)$	$4.4(X-1)$
at $X=78.5$	114	279	342

* The molecular masses are as follows: gas – 40, petrol – 110, diesel fuel – 200, residue – 260; the alkene (olefin):alkane ratio is 0.3.

For example, the heat of catalytic cracking of a feed stock with a molecular mass of 210 in the absence of unreacted feed stock ($Y = 0$) will be:

$$q_{pr} = 71.5\left[\frac{210-16}{210} - \frac{0.113\,(40-16)}{40} + \frac{0.462\,(110-16)}{110} + \frac{0.381\,(200-16)}{200}\,(X - 0.18\times 5.6 - 0.68\times 0)\right.$$

$$\times(0.018 + 2.55\times 0.3 - 1.08\times 0.3^2) = 3.6\,(X-1)$$

At $X = 78.5$, we obtain $q_{pr} = 279$ kJ/kg, i.e. the value given in Table 15.

The extent of cracking can be seen to have the greatest effect on the value of q_{pr}. In the cracking of a light alkane feed stock ($X = 78.5$) and small degrees of conversion, $q_{pr} \approx 115$ kJ/kg, with considerable degrees of conversion $q_{pr} \approx \approx 280$ kJ/kg, while with deeper cracking $q_{pr} \approx 340$ kJ/kg. For a feed stock also containing cycloalkanes and aromatics, the heats are somewhat lower for the reasons indicated above (for example, for light gas oil from petroleum of the Romashkino field, $X = 64$).

Interesting data have been obtained by Orochko and Chernakova [25]. Designating by Y' the sum of the yields of all the products [the same as $(1 - Y)$ above], they obtained the following relations for calculating the heat of catalytic cracking of gas oils in the presence of amorphous (q_a) and crystalline (q_{cr}) zeolite-containing catalysts:

$$q_a = 443.1\,(Y_1)^2 + 70.2Y', \quad q_{cr} = 229.2\,(Y')^2 + 106.2Y'$$

At high degrees of conversion of the feed stock, q_a is 330-370 kJ/kg, while $q_{cr} = 240$-300 kJ/kg. Unlike the last two equations, expression (5.12) for q_{pr} holds for any feed stock and any catalyst.

5.1.2. Platforming

For various variants of the process, we can combine the components by chemical features, which simplifies the calculations of the heat of the process. Platforming is usually characterized by the generalized chemical scheme

$$\mathrm{G} \xleftarrow{w_3} \mathrm{Alk} \underset{w_2'}{\overset{w_2}{\rightleftarrows}} \mathrm{CA} \underset{w_1'}{\overset{w_1}{\rightleftarrows}} \mathrm{A} \qquad \text{(VII)}$$

where G is the gas, Alk is the alkanes, CA is the cycloalkanes, and A is the aromatics; w is the rate of a reaction.

When calculating the heat of a process, how satisfactorily this scheme corresponds to the kinetic data is not important, it is only important that it would enable us to characterize the initial and final mixtures. Although the above scheme takes no account of the reaction of isomerization, the deposition of coke, and some others, the contribution of these disregarded reactions to the total heat of the process is negligibly small (the heats of isomerization are close to zero, while only fractions of a per cent of the feed stock participate in the formation of coke).

Let us consider the method of calculating the heat of a process based on the use of the general scheme of the process and the heats of its steps. We shall assume (which also does not affect the results of calculating the heat) that the process is carried out in an adiabatic ideal-displacement apparatus. Therefore, the equations of the material and heat balances for an elementary volume dv of the apparatus have the form

$$\frac{dn_{\text{Alk}}}{dv} = -(w_2 - w_2') - w_3$$

$$\frac{dn_{\text{CA}}}{dv} = (w_2 - w_2') - (w_1 - w_1')$$

$$\frac{dn_{\text{A}}}{dv} = w_1 - w_1'$$

$$GC_p \frac{dT}{dv} = \Delta H_{\text{CA}\to\text{A}}(w_1 - w_1') + \Delta H_{\text{Alk}\to\text{CA}}(w_2 - w_2') + \Delta H_{\text{Alk}\to\text{G}} w_3$$

where n_i is the molar rate of flow of the i-th component, mol/s; the symbols of the other quantities are the same as above.

By substituting for $(w_1 - w_1')$, $(w_2 - w_2')$, and w_3 in the fourth equation of the above system their values from the first three equations, we obtain an equation in total differentials ($dq_{\text{pr}} = GC_p\, dT$):

$$dq_{\text{pr}} = (\Delta H_{\text{CA}\to\text{A}} + \Delta H_{\text{Alk}\to\text{CA}} - \Delta H_{\text{Alk}\to\text{G}})\, dn_{\text{A}} + (\Delta H_{\text{Alk}\to\text{CA}} - \Delta H_{\text{Alk}\to\text{G}})\, dn_{\text{CA}} - \Delta H_{\text{Alk}\to\text{G}}\, dn_{\text{Alk}}$$

Integration of this equation yields:

$$q_{\text{pr}} = (\Delta H_{\text{CA}\to\text{A}} + \Delta H_{\text{Alk}\to\text{CA}} - \Delta H_{\text{Alk}\to\text{G}})\, n_{\text{A}} + (\Delta H_{\text{Alk}\to\text{CA}} - \Delta H_{\text{Alk}\to\text{G}})\, n_{\text{CA}} - \Delta H_{\text{Alk}\to\text{G}} n_{\text{Alk}} \quad (5.13)$$

The values of $\Delta H_{\text{CA}\to\text{A}}$ and $\Delta H_{\text{Alk}\to\text{CA}}$ (see Table 12) do not depend on the conditions of the process and the molecular mass of the feed stock. The value of $\Delta H_{\text{Alk}\to\text{G}}$ requires clarification. If a reaction is associated with the hydrogenolysis of one C—C bond in an alkane molecule, its heat is easily found from Table 12. But under rigid conditions, hydrocracking can proceed with the breaking of several C—C bonds, and the heat of the reaction Alk → G will grow accordingly. Its determination therefore requires investigation of the nature of hydrocracking and will be illustrated in the general case in the following section. For mild platforming (with the breaking of one C—C bond), $\Delta H_{\text{Alk}\to\text{G}}$ is a constant quantity equal to 56 kJ/mol, and q_{pr} is calculated as follows.

We transform Eq. (5.13) by relating it to one kilogramme of the feed stock, introducing the numerical averaged values of the molar heats, and also by expressing Δn_i in terms of the experimentally determined mass fractions of the hydrocarbons in the feed stock $Y_{0,i}$, the catalysate Y_i, in terms of the mass yield of a stable catalysate

λ and the mean molecular masses M_A, M_{CA}, and M_{Alk} of the hydrocarbons of each group.

The above substitutions yield the final equation for determining the heat q_{pr} (in kJ/kg) of the catalytic reforming process at 500 °C:

$$q_{pr} = \frac{\lambda Y_A - Y_{0,A}}{M_A} \times 312 \times 10^3 + \frac{\lambda Y_{CA} - Y_{0,CA}}{M_{CA}} \times 98 \times 10^3 + \frac{\lambda Y_{Alk} - Y_{0,Alk}}{M_{Alk}} \times 56 \times 10^3 \quad (5.14)$$

For our calculations, we must know the mean molecular masses of the alkanes, cycloalkanes, and aromatics. For this purpose, it is first necessary to measure or calculate the mean molecular mass M of the feed stock. For the usual practical problems, we can further find an estimate of the mean number of carbon atoms in a molecule:

$$m \approx \frac{1}{14}(M_A - 2Y_{Alk} + 6Y_A)$$

and assume that

$$M_{Alk} = 14m + 2, \quad M_{CA} = 14m, \quad M_A = 14m - 6$$

We can also use the relations

$$M_{Alk} \approx M + 2, \quad M_{CA} \approx M, \quad M_A \approx M - 6$$

These approximations change the results of accurate calculations by not over 1-2%.

The results of calculating the heats of the reactions of individual hydrocarbons for 500 °C by Eq. (5.14) and by the heats of formation of the reaction mixture components are given in Table 16 (reduced to the feed stock).

Table 16. **Heats of Reactions of Individual Hydrocarbons at 500 °C**

Reaction	Heat of reaction, kJ/kg	
	by Eq. (5.14)	by heats of formation of reaction mixture components
Dehydrocyclization $Alk_7 \rightarrow A_7$	2566	2533
Ditto $Alk_7 \rightarrow CA_7$	418	376
Dehydrogenation $CA_7 \rightarrow A_7$	2132	2207
Hydrocracking $Alk_7 \rightarrow Alk_3 + Alk_4$	560	510
Dehydrocyclization $Alk_{10} \rightarrow A_{10}$	1800	1776
Dehydrogenation $CA_{10} \rightarrow A_{10}$	1530	1467
Dehydrocyclization $Alk_{10} \rightarrow CA_{10}$	295	295
Hydrocracking $Alk_{10} \rightarrow 2Alk_5$	395	405
$Alk_7 + CA_7 \rightarrow 1.3A_7 + 0.7Alk_3 + 0.7Alk_7$	1296	1312

The results of calculating the heats of catalytic reforming processes described in the literature for various feed stocks are given in Table 17.

Table 17. **Heats of Catalytic Reforming Processes Found by Treating Experimental Data by Eq. (5.14)**

Petrol fraction, °C	Composition of feed stock, mass fractions			Yield of catalysate λ	Composition of catalysate, mass fractions			Heat of process q_{pr}, kJ/kg
	$Y_{0,A}$	$Y_{0,CA}$	$Y_{0,Alk}$		Y_A	Y_{CA}	Y_{Alk}	
				Hydroreforming				
90-130	—	0.45	0.55	0.528	0.626	0.010	0.364	518
90-180	0.105	0.501	0.394	0.828	0.662	0.073	0.265	685
65-180	—	—	1.0	0.657	0.219	—	0.781	718
70-155	0.11	0.21	0.68	0.869	0.325	0.145	0.530	360
				Platforming				
85-170	0.081	0.255	0.664	0.89	0.398	0.036	0.566	518
60-120	0.035	0.225	0.740	0.875	0.246	0.067	0.687	378
60-105	0.067	0.262	0.671	0.840	0.372	0.018	0.610	537
105-140	0.115	0.228	0.657	0.869	0.488	0.012	0.500	627
60-85	0.04	0.702	0.294	0.902	0.614	0.061	0.325	1225

Using the data of Table 17, we find the heat of platforming the fraction 85-170 °C, for example, by the expression:

$$q_{pr} = \left(\frac{0.89 \times 0.398 - 0.081}{108} \times 312 + \frac{0.89 \times 0.036 - 0.255}{114} \times 98 + \frac{0.89 \times 0.566 - 0.664}{116} \times 56 \right) 10^3 = 518 \text{ kJ/kg}$$

The denominators contain the molecular masses of aromatics, cycloalkanes, and alkanes whose determination was considered earlier. The value calculated in this way is given in the last column of the table.

The data of Table 17 reveal that platforming at close values of the degree of conversion of a feed stock similar in composition is attended by a greater absorption of heat than hydroreforming. According to available data, the heat of hydroreforming of various kinds of feed stocks depending on the cycloalkane content in them and the content of aromatics in the products can vary from 180 to 700 kJ/kg, and the heat of platforming, from 380 to about 1200 kJ/kg.

5.1.3. Alkane Fraction Hydrocracking

To work out an analytical method of calculating the heats of alkane fraction hydrocracking, we can use the assumption that the main contribution to the heat of the process is made by the reactions

of C—C bond breaking with hydrogenation and isomerization of the formed fragments. These reactions follow the scheme

$$C_nH_{2n+2} + H_2 \rightarrow C_{n-b}H_{2(n-b)+2} + C_bH_{2b+2} \qquad \text{(VIII)}$$

where n and b are the numbers of carbon atoms in the feed stock and one of the products, respectively.

In a real process, the formed fragments can also experience hydrocracking, in turn. As we have already noted, the heat of a reaction for the hydrocarbons of any group does not depend on the molecular mass of the feed stock, but depends only on the temperature of the process and the products formed. In the breaking of one C—C bond and the hydrogenation of the fragments at 800 °C, 61.9 kJ/mol are evolved with the formation of methane and n-alkanes, 51.8 kJ/mol with the formation of n-alkanes, 58.5 kJ/mol with the partial formation of isoalkanes, and 66.8 kJ/mol with the complete isomerization of the products. The heat q'_{pr} of the process is proportional to the number r of broken bonds and the heat of breaking one bond (with hydrogenation and isomerization of the formed fragments). When one mole of the feed stock is converted with the breaking of r C—C bonds and the formation of $(r + 1)$ hydrogenated fragments, we have:

$$q'_{pr} = rq_{pr} \qquad (5.15)$$

It is easy to find the number of broken bonds if we know the molecular masses of the feed stock and the products. Assume, for example, that a complex process of hydrocracking is described by the general equation

$$C_nH_{2n+2} + rH_2 \rightarrow \sum \nu'_i C_iH_{2i+2} \qquad \text{(IX)}$$

where n and i are the mean numbers of carbon atoms in the molecules of the feed stock and products, respectively, and $\sum \nu'_i$ is the number of moles of the products formed from one mole of the feed stock.

The number of C—C bonds in the feed stock is $(n - 1)$, and in one mole of the i-th product it is $(i - 1)$, accordingly. The number r of broken C—C bonds per mole of feed stock is determined by the difference between the number of these bonds in one mole of the feed stock and in the products obtained from it:

$$r = (n-1) - \sum \nu'_i (i-1) \qquad (5.16)$$

It is simple to find the value of i for an alkane fraction from its molecular mass M_i:

$$i = \frac{M_i - 2}{14} \qquad (5.17)$$

By combining Eqs. (5.15)-(5.17), we obtain the following equation for the heat of hydrocracking of an alkane fraction (in kJ/mol):

$$q'_{pr} = \frac{q_{pr}}{14}\left[(M-16) - \sum \nu'_i (M_i - 16)\right] \qquad (5.18)$$

or for one kilogramme of the feed stock and "mass" coefficients ν_i that are the mass yields of the products relative to the feed stock, we obtain (in kJ/kg):

$$q''_{pr} = \frac{q_{pr} \times 10^3}{14M} \left[(M - 16) - \sum \frac{M}{M_i} (M_i - 16) \right] \qquad (5.19)$$

because $q''_{pr} = q_{pr} \times 10^3/M$ and $\nu_i = \nu'_i M_i / M$.

For several processes, we compared the heats of the reactions of individual hydrocarbons with the formation of normal alkanes found from the heats of formation of the reactants and by Eq. (5.19) with the use of the corresponding value of $q_{pr} = -51.8$ kJ/mol. The results showed a high accuracy of the obtained relation.

To calculate real processes when no data on the individual composition of the mixture are available, one must choose the value of q_{pr}. It is known [13, 22] that in the hydrocracking of normal alkanes the formation of methane is negligible, while the ratio of normal and isoalkanes in the products is 1:3. Consequently, for real processes and temperatures of about 400 °C, we can assume that $q_{pr} = -63.1$ kJ/mol. Hence,

$$q''_{pr} = \frac{4514}{M} \left[(M - 16) - \sum \frac{M}{M_i} \nu_i (M_i - 16) \right] \qquad (5.20)$$

For the hydrocracking of *n*-decane, we compared the heats calculated by Eq. (5.20) and from data on the amount and heats of formation of the feed stock and products. The coincidence of the values found in these two ways (535 and 538 kJ/kg) was good. For the hydrocracking of a technical feed stock (the 350-500 °C fraction of Romashkino petroleum), the following yields of the products, which included gas ($M_g = 45$), petrol ($M_p = 130$), diesel fuel ($M_{df} = 215$), and a residue ($M_r = 380$), were obtained under various conditions of the process (in mass fractions):

Gas	Petrol	Diesel fuel	Residue above 350 °C	Heat of process q''_{pr}, kJ/kg of feed stock
—	0.040	0.160	0.800	44.7
0.171	0.510	0.254	0.083	395
0.100	0.154	0.669	0.079	297

In accordance with the equation for q''_{pr}, the total heat of hydrocracking changes with a change in the degree of conversion of the feed stock or in the yields of the various products (i.e. ν_i); for a technical alkane feed stock, it can reach 300-400 kJ/kg.

5.1.4. Hydrocracking of Alkane-Cycloalkane Mixtures

Assume that a fraction containing $Y_{0,Alk}$ alkanes Alk, $Y_{0,CA}$ cycloalkanes CA, and $Y_{0,A}$ aromatics A is subjected to hydrocracking; here Y_0 is measured in mass fractions ($Y_{0,Alk} + Y_{0,CA} +$

$+ Y_{0,A} = 1$). The products of hydrocracking are fractions with a lower boiling point than that of the feed stock, namely, gas, light petrol, etc., and also a residue. The latter is a fraction coinciding in its boiling point with the feed stock, but differing from it in its group composition.

Let us denote by λ_i the yield of the i-th product in mass fractions, and by $Y_{i,Alk}$, $Y_{i,CA}$ and $Y_{i,A}$ ($Y_{i,Alk} + Y_{i,CA} + Y_{i,A} = 1$) the content of alkanes, cycloalkanes, and aromatics in this product. We must stress that the cited quantities λ_i and Y_i are determined when carrying out a process and we can calculate the heat of hydrocracking by using them. Since in the hydrocracking of light fractions the aromatics do not undergo substantial chemical changes [13, 22], when calculating the heat of a process one must take into consideration the conversions of the alkane-cycloalkane part of the feed stock. The treatment of such a case is convenient for understanding the essence of the method.

The method of calculating the heat of a process is based on a chemical scheme of conversion of the feed stock components. Since the heat of a process depends only on the masses of the reactants and products, but not on the number and kind of the intermediate steps, the inaccurate determination of the chemical scheme will not result in an error when determining q.

Let us write the scheme of conversions in the hydrocracking of light fractions in the form:

$$CA_0 \xrightarrow{+H_2} Alk_0 \xrightarrow{+rH_2} \sum \nu_i Alk_i \qquad (X)$$

where the subscript "0" signifies the feed stock hydrocarbons, Alk_i is the alkanes contained in the i-th product, and ν_i is the number of moles of Alk_i formed as a result of the complete decomposition of one mole of Alk_0.

In accordance with scheme (X), the hydrocracking of cycloalkanes leads to the formation of alkanes with the same number of carbon atoms; products with a smaller number of carbon atoms form from alkanes. With such a scheme, there is no need to determine the composition of the products of deep cycloalkane hydrocracking.

We have already indicated that the molar heat of a reaction $q_{CA \to Alk}$ depends only slightly on the molecular mass of the feed stock and can be adopted as constant at the temperatures of an industrial process. The heat of the first step of a process in the treatment of one kilogramme of feed stock is

$$q_1 = \left(n_{0,CA} - \sum n_{i,CA}\right) q_{CA \to Alk}$$

$$= 10^3 \left[\frac{Y_{0,CA}}{M_{0,CA}} - \frac{\sum \lambda_i Y_{i,CA}}{M_{i,CA}}\right] q_{CA \to Alk} \qquad (5.21)$$

where $n_{0,CA}$ and $n_{i,CA}$ are the numbers of moles of cycloalkanes in one kilogramme of the feed stock and the i-th product obtained from it, respectively, and $M_{0,CA}$ and $M_{i,CA}$ are the mean molecular masses of the cycloalkanes in the feed stock and the i-th product, respectively.

The heat q_2 of the second step of the process is determined as follows. The number of moles of alkanes subjected to hydrocracking and related to one kilogramme of processed feed stock, Δn_{Alk}^{calc}, consists of the change in the number of moles of cycloalkanes and alkanes in the process:

$$\Delta n_{Alk}^{calc} = (n_{0,\,CA} - \sum n_{i,\,CA}) + (n_{0,\,Alk} - n_{k,\,Alk})$$

where $n_{0,CA}$ and $n_{i,CA}$ are the same as above, $n_{0,Alk}$ is the number of moles of alkanes in one kilogramme of the feed stock, and $n_{k,Alk}$ is the same in the product coinciding in its boiling points with the feed stock and indicated by the subscript k.

Using the experimental values, we obtain:

$$\Delta n_{Alk}^{calc} = 10^3 \left[\left(\frac{Y_{0,\,CA}}{M_{0,\,CA}} - \sum \frac{\lambda_i Y_{i,\,CA}}{M_{i,\,CA}} \right) + \left(\frac{Y_{0,\,Alk}}{M_{0,\,Alk}} - \frac{\lambda_{Alk} Y_{k,\,Alk}}{M_{k,\,Alk}} \right) \right]$$

Therefore for the heat of the second step of the process, we have:

$$q_2 = 10^3 \left[\left(\frac{Y_{0,\,CA}}{M_{0,\,CA}} - \sum \frac{\lambda_i Y_{i,\,CA}}{M_{i,\,CA}} \right) + \left(\frac{Y_{0,\,Alk}}{M_{0,\,Alk}} - \frac{\lambda_{Alk} Y_{k,\,Alk}}{M_{k,\,Alk}} \right) \right] r q_{Alk \to Alk_i} \qquad (5.22)$$

where $q_{Alk \to Alk_i}$ is the heat of hydrogenolysis of one C—C bond in alkanes (it is determined by the thermodynamic properties of the reactants and is given in Table 12), and r is the mean number of broken C—C bonds in an alkane molecule [for the calculation of r see Eq. (5.16)].

Combining expressions (5.21) and (5.22) for q_1 and q_2, we obtain the following formula for calculating the heat of hydrocracking:

$$q_{pr} = q_1 + q_2 = q_{CA \to Alk} (n_{0,\,CA} - \sum n_{i,\,CA}) + q_{Alk \to Alk_i} \Delta n_{Alk}^{calc} r \qquad (5.23)$$

To verify the accuracy of the proposed expression (5.23), we have compared calculations by it with the exact determination of q from the heats of formation of the reactants for a number of model examples. Assume that a mixture of 50% (by mass) of n-heptane and 50% (by mass) of methylcyclohexane is subjected to hydrocracking. As a result, we obtain 50% each (by mass) of a gas and a liquid, the gas containing equal concentrations of propane and isobutane, and the liquid, equal concentrations of the initial hydrocarbons. For this example, calculations by Eq. (5.23) yield $q_{pr} = -326$ kJ/kg, whereas exact calculations from the heats of formation of the reactants

at 500 °C yield q_{pr} = —331 kJ/kg, i.e. the coincidence gives the accuracy needed for practical purposes. Table 18 gives the results of calculating the heats of hydrocracking of a heavy petrol fraction for a various degree of conversion of the feed stock. The hydrocracking was performed to obtain low-boiling alkanes.

Table 18. **Heats of Hydrocracking of Petrol at a Pressure of 5 MPa***

Item	Regime (temperature, volume rate of feed)			
	360 °C, 2 h^{-1}	370 °C, 2 h^{-1}	380 °C	
			2 h^{-1}	0.5 h^{-1}
Yield, mass fractions:				
gas	0.075	0.175	0.200	0.302
hydrogenate	0.185	0.375	0.365	0.398
residue	0.74	0.45	0.435	0.300
Molecular mass:				
gas	50.0	51.6	51.8	51.1
petrol	78.0	80.0	76.4	75.0
Content in residue, mass fractions:				
alkanes	0.530	0.520	0.451	0.474
cycloalkanes	0.238	0.216	0.185	0.140
Cycloalkane content in hydrogenate, mass fractions	0.158	0.141	0.130	0.099
$-q_1$, kJ/kg	42.6	27.6	35.1	52.7
r, kJ/kg	1.20	1.20	1.25	1.39
q_2, kJ/kg	118.7	250.8	334.4	401.3
$-q_{pr}$, kJ/kg	123.7	278.4	369.5	454.0

* The following values were used in the calculations: $M_{0,Alk} = 131.7$, $M_{0,CA} = 129.7$, $Y_{0,Alk} = 0.582$, $Y_{0,A} = 0.143$, $q_{CA \to Alk} = -41.8$ kJ/mol, and $q_{Alk \to Alk_i} = -63.1$ kJ/mol.

Inspection of the data in Table 18 reveals that as the regime of the process becomes more rigid, the number of broken bonds per molecule increases from 1.2 to 1.4. The heats of hydrocracking calculated by formula (5.23) reflect this relation and show that the main heat is evolved owing to the decomposition of alkanes. The fraction of heat introduced as a result of breaking of the cycloalkane ring is close to 10% of the total heat of the process. The latter fluctuates depending on the extent of the process from —125 to —455 kJ/kg so that thermal instability is possible [8].

5.1.5. Hydrofining

In hydrofining processes, the hydrogenolysis of C—S bonds is performed with the formation of hydrocarbons and hydrogen sulphide. The heats of hydrogenolysis of C—S bonds are quite significant

and are compatible with those of the hydrogenolysis of C—C bonds (see Table 12), which is illustrated by the following data on the heats of hydrogenolysis of C—S bonds in sulphides and thiols [26] (in kJ/mol):

	at 800 K	at 900 K
$(C_3H_7)_2S \xrightarrow{+H_2} n\text{-}C_6H_{14} + H_2S$	−70.0	−72.1
$(C_4H_9)_2S \xrightarrow{+H_2} n\text{-}C_8H_{18} + H_2S$	−69.1	−71.3
$C_6H_{13}SH \xrightarrow{+H_2} n\text{-}C_6H_{14} + H_2S$	−66.7	−68.7
$C_8H_{17}SH \xrightarrow{+H_2} n\text{-}C_8H_{18} + H_2S$	−66.7	−68.5

The heat of hydrogenolysis of C—S bonds can be seen to change only slightly with the temperature for different sulphur-containing compounds. If the concentration of sulphur compounds in hydrofining were considerable, it would be necessary to take into account the contribution of the reactions of C—S bond hydrogenolysis to the total heat of the process. But in the production of motor fuels, the concentration of sulphur compounds is low (generally less than 0.5%), and even with the complete hydrogenolysis of all the C—S bonds the evolved heat is less than 0.5 kJ/mol of processed petroleum fraction. Such an evolution of heat does not naturally affect the thermal and kinetic regime of the process, and it may be disregarded. The heat of hydrogenolysis of C—S bonds has to be considered for the hydrofining of boiler fuel obtained from the fuel-oil residues of sulphurous petroleums. In this case, the sulphur compounds have a high concentration, and their transformations must be taken into account in heat calculations.

In the hydrofining of petrols, jet and diesel fuels, the non-isothermal nature of the processes is a result not of reactions of hydrogen sulphide evolution, but of ones of hydrogenation and hydrocracking of hydrocarbons. Let us illustrate this using the example of the hydrofining of a petrol fraction containing 0.2% of sulphur compounds and completely purified of them. In hydrofining, there is also formed about 2% of hydrocarbon gases owing to the hydrocracking of the hydrocarbons. In this case, and it characterizes the technical process of hydrofining of petrols directed for platforming, the heat evolved at the expense of hydrocracking is ten times greater than the heat of hydrogenolysis of the C—S bonds (it is assumed that the heats of hydrogenolysis of C—C and C—S bonds are close).

Thus, the heat of the hydrofining of light petroleum fractions can be determined by using the methods of calculating the heats of hydrocracking processes treated above.

Below we shall consider a method of calculating the heats of hydrofining-hydrocracking of heavy petroleum fractions with a consider-

able sulphur compound content. In heavy petroleum fraction hydrofining-hydrocracking processes, the reactions proceeding include the hydrogenation of polycyclic aromatic compounds, hydrocracking, and hydrogenolysis of C—S bonds. We usually do not succeed in obtaining reliable data on the change in the individual structures during a process. It is therefore difficult to employ data on the heats of reactions of individual structures.

In this connection, we have proposed a simplified method for calculating the heats q_{pr} of the hydrogenation treatment of petroleum fractions in which the two main trends are taken into consideration, namely, hydrocracking with the formation of low-boiling hydrocarbons and hydrogenolysis with the evolution of H_2S. This method is based on using the equation

$$q_{pr} = \Delta H_b \Delta z_b + \Delta H_S (-\Delta z_S) \qquad (5.22')$$

where ΔH_b is the heat of formation of a unit mass of the low-boiling (in comparison with the feed stock) hydrocarbons, Δz_b is the change in the content of these hydrocarbons, ΔH_S is the heat of removal of a unit mass of the sulphur, and Δz_S is the change in the sulphur content.

The use of Eq. (5.22′) presumes that the values of Δz_b and Δz_S have been measured. As regards ΔH_b and ΔH_S, these quantities cannot be chosen by analogy with the reactions of individual substances, as was done previously, and must be found from the results of an experiment with the measurement of q_{pr}.

The heats of hydrodesulphurizing-hydrocracking of heavy residues have been measured by Iishii *et al* [27], and their results are presented in Table 19. These data can be used for heat calculations; however, it is prudent on their basis to determine ΔH_b and ΔH_S and then obtain an expression for calculating the heat of a process q_{pr}.

An analysis of the data of Table 19 reveals that there is a correlation between the heat of a process and the amounts of the formed products of hydrocracking and removed sulphur. At the same time, there is no correlation between the heat of a reaction and the expenditure of hydrogen, which, true, may be associated with the errors in determining this expenditure. Thus, the data of Table 19 support the use for calculations of the dependence of the heat of a process in the form of Eq. (5.22′), but not in the form of an equation expressing q_{pr} as a function of the hydrogen expenditure, which Iishii *et al* [27] attempted to do.

Processing of the data of Table 19 by Eq. (5.22′) using the method of least squares yielded ΔH_b and ΔH_S. Here we resorted to different samples.

It was found that ΔH_b varies from —109 to —121 kJ/kg of decomposed feed stock, and ΔH_S varies from —5420 to —5630 kJ/kg of removed sulphur. For calculations of the heats of the processes,

Table 73 Heats of Heavy Petroleum Fraction Desulphurizing Processes [27]

Item	Density ρ^{15} (kg/m³) and sulphur content z_S (mass fractions) in fraction being processed										
	$\rho^{15} = 990$, $z_S = 0.044$					$\rho^{15} = 940$, $z_S = 0.025$	$\rho^{15} = 930$, $z_S = 0.011$	$\rho^{15} = 960$, $z_S = 0.04$			$\rho^{15} = 970$, $z_S = 0.027$
Conditions of process:											
temperature, °C	425	425	430	435	440	425	425	425	435	440	425
pressure, MPa	12	20	20	20	19	20	20	20	20	20	20
Results of process:											
yields, % (mass)											
gas	0.6	1.3	2.6	2.5	—	0.4	0.3	1.0	0.8	1.0	0.6
fraction C_5—300 °C	16.0	15.8	28.8	28.2	44.0	13.0	12.7	18.3	21.7	17.5	13.8
fraction above 300 °C	83.4	82.9	69.8	69.3	56.0	86.6	87.0	80.7	77.5	81.5	85.6
amount of removed sulphur, %	11.0	67.5	76.2	82.4	90.5	49.2	37.1	75.0	84.3	85.5	70.3
expenditures of hydrogen, mol/kg	0.3	2.5	2.7	2.9	2.8	1.3	0.6	2.5	2.8	2.9	1.5
Heat of process, kJ/kg											
experimental	—	188	226	226	280	171	21	167	218	197	100
calculated	—	188	241	225	277	69	—	—	—	—	—

we chose the values of $\Delta H_b = -115$ kJ/kg and $\Delta H_S = -5525$ kJ/kg. These values were compared with the heats of similar reactions of individual substances whose molecular mass is close to that of the heavy petroleum fractions. For example, for the reaction of hydrocracking of acenaphthene with the formation of tetralin and methylcyclohexane and a 30% conversion of the feed stock, the heat of the reaction (similar to ΔH_b) is —120 kJ/kg of the decomposition products, while for the hydrogenolysis of benzthiophene with the formation of diphenyl and hydrogen sulphide, the heat of the reaction (similar to ΔH_S) is —5501 kJ/kg of removed sulphur. The closeness of the heats of the reactions of individual substances and of the found values of ΔH_b and ΔH_S also substantiates the use of the latter for calculating the heats of technical processes.

Thus, if q_{pr} relates to one kilogramme of the feed stock being processed, ΔH_b to one kilogramme of the decomposition products, and ΔH_S to one kilogramme of the removed sulphur, we obtain (in kJ/kg):

$$q_{pr} = -115\Delta z_b + 5525\Delta z_S \qquad (5.23')$$

Since $\Delta z_b > 0$ and $\Delta z_S < 0$ (the sulphur content diminishes), both terms of this equation are negative. We have calculated the values of q_{pr} for different variants of hydrofining-hydrocracking of fuel oil residue and deasphaltized tar. In our investigations, by changing the regime parameters, we succeeded in controlling the extent of hydrocracking and hydrofining. The selectivity of the hydrocracking increased with elevation of the process temperature to 420 °C. The removal of the sulphur compounds was facilitated by a relatively low (370 °C) temperature and high (up to 3000) circulation turnover. Some results of the calculations are presented in Table 20.

It can be seen from the data in Table 20 that in heavy fraction hydrofining processes with a small extent of hydrocracking the reactions of hydrogenolysis of the C—S bonds make the main contribution to the heat of a process. For example, in the purification of sulphurous fractions (a sulphur content in the feed stock of 4% and more) with the production of a low-sulphur (up to 1% of sulphur) furnace fuel and low hydrocracking (up to 10-15% of light products), the evolution of heat is about 180 kJ/kg of the feed stock, about 90% of this value falling to the share of the hydrogenolysis of the C—S bonds.

In the hydrofining of heavy kinds of feed stock, compounds of oxygen and nitrogen in addition to those of sulphur are subjected to hydrogenolysis. Below we compare the heats of hydrogenolysis of selected compounds at 800 K:

Hydrogenolysis reaction	Heat of hydrogenolysis, kJ/mol
$C_6H_{13}SH + H_2 \rightarrow C_6H_{14} + H_2S$	—69
$C_6H_{13}OH + H_2 \rightarrow C_6H_{14} + H_2O$	—93
$C_6H_{13}NH_2 + H_2 \rightarrow C_6H_{14} + NH_3$	—87

Table 20. **Heats of Heavy Petroleum Fraction Hydrofining-Hydrocracking Processes (Hydrodesulphurization) Calculated by Eq. (5.24) (at pressure of 15 MPa)**

Material, conditions	Yield of decomposition products (distillate fractions), mass fractions Δz_b	Change in sulphur content, mass fractions Δz_S	Heat of process, kJ/kg		
			total	at expense of hydrocracking ($-115\Delta z_b$)	at expense of hydrogenolysis of C—S bonds ($5525\Delta z_S$)
Romashkino petroleum fuel oil residues, $z_S = 0.025$, at 370—420 °C, volume flow rate 1.0 h^{-1}, circulation turnover 1500 m^3/m^3	0.14	0.003	—32.7	—16.1	—16.6
	0.48	0.006	—88.2	—55.0	—33.2
	0.10	0.015	—94.4	—11.5	—82.9
	0.20	0.016	—111.4	—23.0	88.4
Fuel oil residues of mixture of Western Siberian petroleums, $z_S = 0.026$ at 380-425 °C, volume flow rate 0.5 h^{-1}, circulation turnover 1000 m^3/m^3	0.08	0.017	—103.1	—9.2	—93.9
	0.17	0.015	—102.5	—19.6	82.9
	0.275	0.015	—114.5	—31.6	—82.9
Arlan petroleum tar, $z_S = 0.04$, at 380-420 °C, volume flow rate 0.5 h^{-1}, circulation turnover 1000 m^3/m^3	0.09	0.03	—176.2	—10.4	—165.8
	0.10	0.03	—177.3	—11.5	—165.8
	0.13	0.03	—180.8	—15.0	—165.8

Both in the reactions given above and in various other reactions of a single type, the hydrogenolysis of C—O and C—N bonds proceeds with a greater evolution of heat than for C—S bonds. At the temperatures of technical processes, the increase in the evolution of heat is about 14%. Consequently, when calculating the heats of hydrofining with the removal of noticeable amounts of oxygen- and nitrogen-containing compounds, we can use formula (5.23′) after including in it a term taking into account the change in the oxygen and nitrogen content (in fractions of the feed stock) Δz_{O+N} and the heat of their removal (per kilogramme of the removed elements) ΔH_{O+N}. We estimate the latter quantity to be 1.14 ΔH_S. As a result, we find (in kJ/kg):

$$q_{pr} = -115\Delta z_b + 5525\Delta z_S + 6230\Delta z_{O+N} \qquad (5.24)$$

For example, if in the hydrogenation of Arlan petroleum tar (see Table 20), 13% of the feed stock is subjected to hydrocracking

($\Delta z_b = +0.13$), the change in the sulphur content is 3% ($\Delta z_s = -0.03$), and in the nitrogen and oxygen content it is 1% ($\Delta z_{O+N} = -0.01$). The evolution of heat is —243 kJ/kg, i.e. it will be greater by 62 kJ/kg than when the oxygen and nitrogen are not removed.

5.1.6. Coking and Technical Carbon Production Processes

In the processes of coking and the production of technical carbon from liquid or gaseous hydrocarbons, a solid material enriched in carbon forms. The heats of producing one kilogramme of carbon from hydrocarbons of the formula C_nH_m when they decompose into carbon and hydrogen, q_{pr} (in kJ per kilogramme of carbon) can easily be calculated from the heats of formation ΔH_f°:

$$q_{pr} = -\Delta H_f^\circ \frac{1000}{12n} \tag{5.25}$$

The values of q_{pr} at 300 K (they do not change very greatly with the temperature) are given in Table 21.

Table 21. **Heats Evolving in the Decomposition of Hydrocarbons with the Formation of Carbon at 300 K**

Hydrocarbon	Heat of producing 1 kg of carbon in the decomposition of hydrocarbons to carbon and hydrogen, q_{pr}, kJ/kg
Methane, CH_4, gas	6240
Ethane, C_2H_6, gas	3530
Propane, C_3H_8, gas	2890
n-Pentane, C_5H_{12}, gas	2440
Ethylene, C_2H_4, gas	—2180
Propylene, C_3H_6, gas	—570
1-Butene, C_4H_8, gas	20
Cyclopropane, C_3H_6, gas	—1960
Acetylene, C_2H_2, gas	—9450
Methylacetylene, C_3H_4, gas	—5150
Allene, C_3H_4, gas	—5340
Benzene, C_6H_6, gas	—1150
Ditto, liquid	—680
Naphthalene, $C_{10}H_8$, gas	—1270
Ditto, solid	—650

The data given in Table 21 reveal that the complete decomposition of alkanes to simple substances proceeds with a considerable absorption of heat ($q_{pr} > 0$), of dienes and acetylenes—with a considerable evolution of heat, and of alkenes and aromatics—with the evolution of a small amount of heat.

When calculating technical processes, one must have in view that the formed coke or technical carbon contains a certain amount of hydrogen (their structural formula is CH_a), and also that the decomposition of the feed stock is attended by complicated processes leading to the formation of hydrocarbons. Table 22, for example, gives the products obtained in the coking of selected kinds of feed stock.

Table 22. **Product Yields in the Coking of Selected Kinds of Feed Stock**

Feed stock	Yield, % (mass)				
	gas	petrol	light gas oil	heavy gas oil	coke
Fuel oil residue	4.7	7.8	42	30	15.5
Heavy tar	7.2	16.5	27.3	23.5	24.5
Cracking residue	8.3	7.3	12.4	36	36

Let us attempt to estimate the heats of these processes from the heats of combustion of the feed stock and products. Approximate values must never be used. Assume, in accordance with [21], that the heats of combustion (in kJ/kg) of the fuel oil residue is 41 200, of the tar is 39 950, of the cracking residue and gas oils is 40 160, of the gas is 47 200, of the petrol is 44 200, and of the coke is 33 500 (all the values are negative). We find that with these values the heats of coking for the balances in Table 22 range from —700 to —1400 kJ/kg. If, for example, the heats of combustion of gas oils are adopted equal to 42 500, and of the coke to 35 000 (these values are also cited in the literature), then, for example, in the coking of the cracking residue the heat of the process is +154 kJ/kg. Here the need in a high accuracy of determining the heats of combustion noted at the beginning of this chapter is confirmed. A sufficiently accurate relation for calculating the heats of combustion (in kJ/mol) of a gaseous hydrocarbon having the composition C_nH_m has the form [28]:

$$\Delta H_c^\circ = -(204.2n + 44.4m + \sum x_i) \qquad (5.26)$$

where $\sum x_i$ are corrections taking the structure of the hydrocarbon into account.

The heat of combustion $\Delta H_{c,c}^\circ$ of coke having the composition CH_a will be estimated from its heat of formation (10.86a kJ/mol) and the heats of formation of CO_2 (—393.5 kJ/mol) and water (—242.2 kJ/mol):

$$\Delta H_{c,c}^\circ = \Delta H_f^\circ(CO_2) + \frac{a}{2}\Delta H_f^\circ(H_2O) - \Delta H_f^\circ(CH_a)$$
$$= -393.5 - 132a \qquad (5.27)$$

Let us apply these equations for approximate estimates of the heat of coking.

Assume that in the coking of the feed stock C_nH_m hydrocarbons of the composition $C_{n_1}H_{m_1}$ (their mass yield is ν_h) and coke of the composition CH_a (its mass yield is $\nu_c = 1 - \nu_h$) form. The balance equation is

1000 g of feed stock → 1000 ν_h of hydrocarbons + 1000 ν_c of coke

or (in moles):

$$\frac{10^3}{M_{fs}} C_nH_m \rightarrow \frac{(1-\nu_c)\,10^3}{M_h} C_{n_1}H_{m_1} + \frac{\nu_c \times 10^3}{12+a} CH_a \qquad \text{(XI)}$$

where M_{fs} and M_h are the molecular masses of the feed stock and the sum of the product hydrocarbons, respectively.

We shall determine the values of m_1 and n_1 from the carbon balance (the equality of the number of carbon moles in the feed stock and the products):

$$\frac{n}{M_{fs}} = \frac{1-\nu_c}{M_h} n_1 + \frac{\nu_c}{12+a}$$

whence

$$n_1 = \left(\frac{n}{M_{fs}} - \frac{\nu_c}{12+a}\right) \Big/ \left(\frac{1-\nu_c}{M_h}\right) \qquad (5.28)$$

$$m_1 = M_h - 12n_1 \qquad (5.29)$$

The heat of coking q_c for stoichiometric equation (XI) is (in moles)

$$q_c = \frac{10^3}{M_{fs}} \Delta H_c^\circ (C_nH_m) - \frac{(1-\nu_c)\,10^3}{M_h} \Delta H_c^\circ (C_{n_1}H_{m_1}) - \frac{\nu_c \times 10^3}{12+a} \Delta H_c^\circ (CH_a) \qquad (5.30)$$

Introducing into Eq. (5.30) the expressions of the heats of combustion ΔH_c° of the components, the values of n_1 and m_1 from Eqs. (5.28) and (5.29), and having in view that from Eq. (5.29) $M_h = 12n_1 + m_1$, we arrive at an expression of the form

$$q_c = 10^3 \frac{\nu_c}{12+a} (C_1 + C_2 a) \qquad (5.31)$$

An estimate of the constants C_1 and C_2 without account taken of corrections yields values of 189 and 88, respectively. But both the feed stock and the hydrocarbon products contain vinyl and phenyl groups and cycloalkane rings for which corrections are introduced. The taking into account of the corrections requires the determination of the number of these structures per molecule. For coking and the production of carbon black from thermal gas oil, the consideration of the relevant corrections results in the expression

$$q_c \approx \frac{10^3 \nu_c}{12+a} (48 + 18a) \qquad (5.32)$$

If, for example, the coke yield is 30% ($\nu_c = 0.3$) and the composition of the coke is $CH_{0.5}$ ($a = 0.5$), we have $q_c = 1370$ kJ/kg.

Expression (5.32) is an approximate one. It is good practice to calculate the heats of a process from the heats of formation of the substances. But for this purpose it is necessary to introduce group components (see above), which is possible if the chemical composition of the feed stock and products is known.

Hence, calculations of the heat of coking require: (1) a choice of the model group components characterizing the feed stock and the products; (2) the determination of the heats of formation of the group components and coke from tables or relations for ΔH_f°; and (3) calculations of the heat of the process from the found heats of formation.

Assume, for example, that in the coking of one kilogramme of butylbenzene we obtained approximately the same product yields as from cracking residue, the gas consisting of ethylene, the petrol—of benzene, the light gas oil—of naphthalene ($C_{10}H_8$), the heavy gas oil—of diphenyl ($C_{12}H_{10}$), and the composition of the coke is $CH_{0.4}$ (it is taken into account that the coking products are aromatized). Here the balance of the process for one kilogramme of feed stock (7.5 moles) calculated for the amount of substance in moles and taking into account the evolution of the excess hydrogen is:

$$7.5C_{10}H_{14} \rightarrow 21H_2 + 3.5C_2H_4 + 1.0C_6H_6 + 1.0C_{10}H_8 + 2.3C_{12}H_{10} + 24.4CH_{0.4}$$

The heats of formation of the hydrocarbons are given in thermodynamic tables, they can be determined using the relations or methods contained herein (see Appendix 1). For the heat of formation of coke having the composition CH_a at 298 K, we find (see p. 247) $\Delta H_{f,298}^\circ = 10.86a$ kJ, and for $a \approx 0.4$, we obtain $\Delta H_{f,298}^\circ = 4.3$ kJ. Thus, the heat of the model process is

$$q_c \approx 3.5 \times 52.3 + 1.0 \times 83.0 + 1.0 \times 152.0 + 2.3 \times 172.9 + 24.4 \times 4.3 - 7.5\,(-13.8) = 1024 \text{ kJ}$$

Consequently, if the coking products contain aromatics, coking requires the supply of heat although the decomposition of the feed stock into C and H_2 is exothermic.

It should be noted that in the above calculations the heat of coking is higher than for a technical feed stock because both the feed stock and the products contain alkanes and cycloalkanes. If we consider that the content of the non-aromatic hydrocarbons is 40%, the heat of the process will lower to 150-200 kJ/kg of feed stock, which is close to the estimates obtained on the basis of an approximate heat balance of an industrial reactor—from 120 to 170 kJ/kg of feed stock [29].

The calculations are performed similarly for processes of technical carbon production when liquid hydrocarbon fractions are the feed

stock. On the other hand, when methane is the feed stock, the calculations are performed as for a simple chemical reaction.

In some techniques of producing technical carbon, partial oxidation of the feed stock or gaseous fuel is used to compensate for the heat of the process. An approximate calculation of the heat balance is possible because the thermal characteristics including the heat of the process are estimated with a low accuracy.

The heat of combustion q_c of the fuel goes to heat the combustion products (q_{ht_1}), the coking feed stock (q_{ht_2}) to the reaction temperature, and to compensate for the heat q_{pr} of the process:

$$-q_c = q_{ht_1} + q_{ht_2} + q_{pr}$$

The object of the calculations is to determine the amount of feed stock spent on combustion.

In essence, the calculations can be performed as for a complex adiabatic reaction (see Chap. 4), but since the value of q_{pr} is known with a substantial error, they can be simplified. This is done by writing the heat balance not for an elementary temperature interval from T to $T + dT$, but for the entire temperature interval from the initial one T_0 to the reaction one T_r.

Let us illustrate these calculations for the case when methane is the feed stock for both combustion and producing carbon, and air is the oxidizing agent. The heat of the reaction $CH_4 \rightarrow C + 2H_2$ is 74.9 kJ/mol, while the heat of combustion of methane is $q_c = -890$ kJ/mol. Let the mole fraction of the burning methane be x (mol/mol). For combustion ensuring the decomposition of one mole of CH_4, we need $2x$ moles of oxygen, and the air with this amount of it will contain $3.76 \times 2x = 7.52x$ moles of nitrogen. The combustion products contain x moles of CO_2, $2x$ moles of H_2O, $7.52x$ moles of N_2, 1 mole of CH_4, and must be heated from $T_0 = 300$ K to $T_r = 1500$ K. Hence

$$q_{ht_1} + q_{ht_2} = [\bar{C}_p\,(CO_2)\,x + \bar{C}_p\,(H_2O)\,2x + \bar{C}_p\,(N_2)\,7.52x + \bar{C}_p\,(CH_4)]\,(T_r - T_0)$$

(here the bar indicates the mean molar heat capacities). We find

$$q_{ht_1} + q_{ht_2} = (50.4x + 39.7 \times 2x + 31.7 \times 7.52x + 65.3)\,(1500 - 300) \times 10^{-3}$$
$$= 441.8x + 78.4 \text{ kJ}$$

We write the heat balance:

$$890x = 441.8x + 78.4 + 74.9$$

whence

$$x = \frac{153.3}{448.2} = 0.34$$

Thus, 0.34 mol (kg) of methane has to be burned per mole (kg) of methane being decomposed to carbon.

It is not difficult to perform similar calculations for any kinds of feed stock.

5.2. Petrochemical Processes

Above we have treated the calculations of the heats of petroleum refining processes. In the petrochemical and chemical industry involved in the processing of hydrocarbon feed stock, problems also

arise of calculating the heats of complex processes because side reactions proceed in addition to the main one. For example, in the isomerization of hydrocarbons, both the reactant and the product are cracked if the process is performed in the absence of hydrogen, or hydrocracked if the process is performed with the introduction of hydrogen. The alkylation of an *n*-alkane or aromatic with alkenes carried out for the production of a monoalkyl-substituted compound is attended by the formation of polyalkyl derivatives. Oxidation processes are still less selective. One of the leading processes of petrochemistry—pyrolysis—uses a complex mixture consisting of the petrol or gas oil fraction as the feed stock. The calculations of the heats of petrochemical processes are easier to perform in comparison with petroleum refining ones because the standard thermodynamic functions of the reactants and products—individual substances—can often be used. For these processes too, however, working relations enabling one to determine the heat of a process with various conversions of the feed stock and selectivities of formation of different products are very convenient. These relations are obtained in the same ways as for petroleum refining processes. Thus, the heat of pyrolysis can be calculated by the same scheme as the heat of cracking (see Sec. 5.1.1) if the indices of no importance for pyrolysis are disregarded (the isoalkane:normal alkane ratio, etc.) and the heats of cracking with the formation of C_2—C_4 alkenes are taken into consideration.

Below we illustrate the obtaining of working relations for complex petrochemical processes of isomerization, alkylation, and oxidation. Data on the heats of the simple steps of petrochemical processes and on their equilibrium constants and equilibrium composition are given in the following chapters.

5.2.1. Isomerization

When analysing industrial isomerization processes, we can limit ourselves to comparatively simple schemes with the participation of two or three isomers in mutual conversions and the participation of each of them in cracking or hydrocracking reactions.

Scheme 1 (used for calculating isomerization processes with the participation of two isomers, for example the production of isobutane from *n*-butane, isopentane from *n*-pentane, etc.):

$$\begin{array}{ccc} A_1 & \underset{w_{21}}{\overset{w_{12}}{\rightleftarrows}} & A_2 \\ w_{1c}\downarrow & & \downarrow w_{2c} \\ & \text{Hydrocracking or cracking products} & \end{array} \qquad (1)$$

Scheme 2 (used for calculating isomerization processes with the participation of three isomers, for example the isomerization of *n*-pentane into *iso*- and neopentanes, of *n*-hexane into *iso*- and neohexanes, of *meta*- and *ortho*-xylenes into *para*-xylene, and so on):

$$\begin{tikzcd} A_1 \arrow[r, shift left, "w_{12}"] \arrow[d, "w_{1c}"'] & A_2 \arrow[l, shift left, "w_{21}"] \arrow[r, shift left, "w_{23}"] \arrow[d, "w_{2c}"] & A_3 \arrow[l, shift left, "w_{32}"] \arrow[d, "w_{3c}"] \\ & \text{Hydrocracking or cracking products} & \end{tikzcd} \tag{2}$$

Industrial isomerization reactors are adiabatic ones. It is interesting to determine the change in the temperature ΔT_{ad} in an adiabatic reactor. Since industrial processes are conducted in adiabatic reactors, the calculation of ΔT_{ad} can be used for determining the deviation of the regime from an isothermal one. At substantial values of ΔT_{ad}, sectioning of the reactor is required.

The heat calculations for industrial adiabatic flow reactors with a stationary catalyst bed can be performed using equations for an ideal displacement regime, although the mixing conditions in them may differ from such a regime.

It should be noted that, as will be shown below, data on the kinetics of a process are not needed for calculating ΔT_{ad}, i.e. there is no need to determine the form of the relation $w_{ij} = f(c_i, T)$.

Let us consider a process following scheme 1. Having in view that $A\,dl = dv$ (A is the area, l is the length, and v is the volume of the reactor), while $Avc_i = n_i$ (n_i is the molar flow of the i-th component), let us write down this process mathematically (C_p = const):

$$\left.\begin{aligned} \frac{dn_1}{dv} &= -w_{12} + w_{21} - w_{1c} \\ \frac{dn_2}{dv} &= w_{12} - w_{21} - w_{2c} \\ GC_p\frac{dT}{dv} &+ \Delta H_{12}(w_{12} - w_{21}) + \Delta H_{1c}w_{1c} + \Delta H_{2c}w_{2c} = 0 \end{aligned}\right\} \tag{5.33}$$

where ΔH_{12} is the heat of isomerization, ΔH_{1c} and ΔH_{2c} are the heats of hydrocracking of A_1 and A_2.

Since it is usually impossible to determine which of the lower-boiling products (of hydrocracking) was formed from A_1 and which from A_2, let us assume that $w_{1c} = w_{2c} = w_c$ and $\Delta H_{1c} = \Delta H_{2c} = \Delta H_c$. Summing of the first two equations of system (5.33) yields

$$\frac{dn_1}{dv} + \frac{dn_2}{dv} = -2w_c, \text{ whence } w_c = -\frac{1}{2}\left(\frac{dn_1}{dv} + \frac{dn_2}{dv}\right)$$

Introducing the expression for w_c into the first equation of system (5.33), we find:

$$w_{12} - w_{21} = \frac{1}{2}\left(-\frac{dn_1}{dv} + \frac{dn_2}{dv}\right)$$

Replacing $w_{12} - w_{21}$ and w_c in the heat equation [the third equation of system (5.33)] with their derivatives, we have:

$$GC_p \frac{dT}{dv} + \left(-\frac{1}{2}\Delta H_{12} - \Delta H_c\right)\frac{dn_1}{dv} + \left(\frac{1}{2}\Delta H_{12} - \Delta H_c\right)\frac{dn_2}{dv} = 0$$

The last equation is easily integrated and transforms into a difference equation:

$$\Delta T_{ad} = \left(\frac{1}{2}\Delta H_{12} + \Delta H_c\right)\frac{\Delta n_1}{GC_p} + \left(-\frac{1}{2}\Delta H_{12} + \Delta H_c\right)\frac{\Delta n_2}{GC_p} \quad (5.34)$$

If we are given the mass rate of flow, the heat capacity of the reacting mixture, and the change in its composition in the reactor, then calculations by (5.34) enable us to determine the change in the temperature in the reactor. The values of ΔH_{12} for different isomerization reactions and of ΔH_c for hydrocracking or cracking are easily found by methods of chemical thermodynamics.

Let us consider a process following scheme 2. Going over, as above, to the variables v and n_i, we shall rewrite system (5.33) in the form:

$$\left.\begin{aligned}
\frac{dn_1}{dv} &= -w_{12} + w_{21} - w_{1c} \\
\frac{dn_2}{dv} &= w_{12} - w_{21} - w_{23} + w_{32} - w_{2c} \\
\frac{dn_3}{dv} &= w_{23} - w_{32} - w_{3c} \\
GC_p \frac{dT}{dv} &+ \Delta H_{12}(w_{12} - w_{21}) + \Delta H_{23}(w_{23} - w_{32}) \\
&+ \Delta H_{1c} w_{1c} + \Delta H_{2c} w_{2c} + \Delta H_{3c} w_{3c} = 0
\end{aligned}\right\} \quad (5.35)$$

Let us assume, as previously, that $w_{1c} = w_{2c} = w_{3c} = w_c$ and $\Delta H_{1c} = \Delta H_{2c} = \Delta H_{3c} = \Delta H_c$. Summing of the first three equations of system (5.35) yields:

$$\frac{dn_1}{dv} + \frac{dn_2}{dv} + \frac{dn_3}{dv} = -3w_c$$

whence

$$w_c = -\frac{1}{3}\left(\frac{dn_1}{dv} + \frac{dn_2}{dv} + \frac{dn_3}{dv}\right)$$

Introducing the expression for w_c into the first equation of system (5.35), we find:

$$w_{12} - w_{21} = -\frac{2}{3}\frac{dn_1}{dv} + \frac{1}{3}\frac{dn_2}{dv} + \frac{1}{3}\frac{dn_3}{dv}$$

Introducing the expression for w_c into the third equation of system (5.35), we obtain:

$$w_{23} - w_{32} = -\frac{1}{3}\frac{dn_1}{dv} - \frac{1}{3}\frac{dn_2}{dv} + \frac{2}{3}\frac{dn_3}{dv}$$

Now replacing $(w_{12} - w_{21})$, $(w_{23} - w_{32})$, and w_c in the last equation of system (5.35) with their derivatives, we have:

$$GC_p\frac{dT}{dv} + \left(-\frac{2}{3}\Delta H_{12} - \frac{1}{3}\Delta H_{23} - \Delta H_c\right)\frac{dn_1}{dv} + \left(\frac{1}{3}\Delta H_{12} - \frac{1}{3}\Delta H_{23} - \Delta H_c\right)\frac{dn_2}{dv} + \left(\frac{1}{3}\Delta H_{12} + \frac{2}{3}\Delta H_{23} - \Delta H_c\right)\frac{dn_3}{dv} = 0$$

Integration of the last equation yields

$$\Delta T_{ad} = \left(\frac{2}{3}\Delta H_{12} + \frac{1}{3}\Delta H_{23} + \Delta H_c\right)\frac{\Delta n_1}{GC_p} + \left(-\frac{1}{3}\Delta H_{12} + \frac{1}{3}\Delta H_{23} + \Delta H_c\right)\frac{\Delta n_2}{GC_p} + \left(-\frac{1}{3}\Delta H_{12} - \frac{2}{3}\Delta H_{23} + \Delta H_c\right)\frac{\Delta n_3}{GC_p} \quad (5.36)$$

Thus, for scheme 2 it is also easy to calculate ΔT_{ad} if we are given the material balance of the process and the heats of the steps have been calculated by methods of chemical thermodynamics.

When performing specific calculations by Eqs. (5.34) or (5.36), one must have in view that G and C_p characterize a mixture of hydrocarbons and a hydrogen-containing gas if the latter circulates in the system. Let G_0 and $C_{p,0}$ be the mass rate of flow and the heat capacity of the hydrocarbons, respectively, α be the mass ratio of hydrogen:hydrocarbons, and $C_{p,g}$ be the heat capacity of the circulating gas. Hence

$$G = G_0(1+\alpha), \quad C_p = \frac{1}{1+\alpha}C_{p,0} + \frac{\alpha}{1+\alpha}C_{p,g} \quad (5.37)$$

To characterize the results of the process, it is convenient to use the ratio of the masses of the components and the sum of the hydrocarbons $z_i = n_i M/G_0$, whence

$$\Delta n_i = \frac{G_0}{M}\Delta z_i \quad (5.38)$$

where M is the molecular mass of the isomers.

Introducing Eqs. (5.37) and (5.38) into Eqs. (5.34) and (5.36) for calculating ΔT_{ad}, we find:

for scheme 1:

$$\Delta T_{ad} = \frac{1/M}{(1+\alpha)\left(\frac{1}{1+\alpha} C_{p,0} + \frac{\alpha}{1+\alpha} C_{p,g}\right)} \left[\left(\frac{1}{2}\Delta H_{12} + \Delta H_c\right)\Delta z_1 + \left(-\frac{1}{2}\Delta H_{12} + \Delta H_c\right)\Delta z_2\right] \quad (5.39)$$

for scheme 2:

$$\Delta T_{ad} = \frac{1/M}{(1+\alpha)\left(\frac{1}{1+\alpha} C_{p,0} + \frac{\alpha}{1+\alpha} C_{p,g}\right)} \left[\left(\frac{2}{3}\Delta H_{12} + \frac{1}{3}\Delta H_{23} + \Delta H_c\right)\Delta z_1 + \left(-\frac{1}{3}\Delta H_{12} + \frac{1}{3}\Delta H_{23} + \Delta H_c\right)\Delta z_2 + \left(-\frac{1}{3}\Delta H_{12} - \frac{2}{3}\Delta H_{23} + \Delta H_c\right)\Delta z_3\right] \quad (5.40)$$

Table 23 presents the results of calculating ΔT_{ad} from the data on the material balances of technical processes.

The heats of hydrocracking of normal and isostructures of alkanes, and also of xylenes have been calculated by the methods of chemical thermodynamics. The heats of reactions change insignificantly with the temperature. For the calculations of ΔT_{ad}, the heats of reactions have been determined for the temperature intervals characterizing technical processes. It should be noted that even appreciable changes in the temperature of reactions can change the value of ΔT_{ad} by not more than one kelvin.

The feed stock of isomerization of *n*-alkanes characterized by the quantities z_{10} and z_{20} contains 99% (mass) of normal and 1% (mass) of isoalkanes. The feed stock for the isomerization of xylenes characteristic of technical processes contains (in per cent by mass) 22 of *ortho*-, 50 of *meta*-, and 23 of *para*-isomers.

The amount of circulation water-containing gas characterized by the quantity α has been selected in all cases so that the molar ratio of the H_2 and hydrocarbons being isomerized will equal unity.

Table 23 also gives equations allowing us to calculate ΔT_{ad} for various changes in the composition of the feed stock. The coefficients of these equations have been determined from the values of ΔH, α, and C_p given in the table in accordance with Eq. (5.39) (for two isomers—scheme 1) or (5.40) (for three isomers—scheme 2).

For the isomerization of virtually pure *n*-butane and *n*-pentane characterized by a slightly exothermic nature at high degrees of conversion and the absence of hydrocracking, the values of ΔT_{ad} do not exceed 20-25 kelvins. Such an elevation of the temperature in one reactor is quite permissible. If a part of the feed stock is subjected to hydrocracking (a highly exothermic process), the values of ΔT_{ad} grow, and after the hydrocracking of 5% of the feed stock, it

Table 23. **Calculated Data on the Adiabatic Change in the Temperature ΔT_{ad} in Isomerization Reactors with a Stationary Catalyst Bed**

Process, scheme	Mass ratio, fractions: component and sum of hydrocarbons in products z_1	z_2	z_3	circulating gas and hydrocarbons α	Heat capacity, kJ/(kg·K): hydrocarbons $C_{p,0}$	circulating gas $C_{p,g}$	Fraction of hydrocracked feed stock, %	ΔT_{ad}, K
Isomerization of butanes* ($M=58$)	By formula (5.39): $\Delta T_{ad} = -319\,\Delta z_1 - 277\,\Delta z_2$							
n-$C_4 \rightleftarrows$ *iso*-C_4	0.50	0.50	—	0.092	2.93	3.95	0	21
↓ ↓	0.50	0.48	—	"	"	"	2	26
	0.50	0.45	—	"	"	"	5	34
Cracking products	0.60	0.40	—	"	"	"	0	16
Isomerization of pentanes** ($M=72$)	By formula (5.39): $\Delta T_{ad} = -425\,\Delta z_1 - 377\,\Delta z_2$							
n-$C_5 \rightleftarrows$ *iso*-C_6	0.50	0.50	—	0.074	1.68	3.95	0	24
↓ ↓	0.50	0.48	—	"	"	"	2	31
	0.50	0.45	—	"	"	"	5	42
Hydrocracking products	0.60	0.40	—	"	"	"	0	19
Isomerization of hexanes*** ($M=86$)	By formula (5.40): $\Delta T_{ad} = -400\,\Delta z_1 - 360\,\Delta z_2 - 289\,\Delta z_3$							
n-$C_6 \rightleftarrows$ *iso*-$C_6 \rightleftarrows$ *neo*-C_6	0.50	0.50	0	0.061	1.66	3.95	0	20
↓ ↓ ↓	0.50	0.40	0.10	"	"	"	0	27
	0.50	0.49	0.01	"	"	"	1	23
Hydrocracking products	0.50	0.41	0.09	"	"	"	0	30
Isomerization of xylenes**** ($M=106$)	By formula (5.40): $\Delta T_{ad} = -278.5\,\Delta z_1 - 269\,\Delta z_2 - 270\,\Delta z_3$							
Ortho $\rightleftarrows$ *Meta* $\rightleftarrows$ *Para*	0.30	0.35	0.30	0.050	1.30	3.95	0	—1
↓ ↓ ↓	0.35	0.25	0.35	"	"	"	0	—1.5
	0.35	0.24	0.35	"	"	"	1	2
Hydrocracking products	0.35	0.22	0.35	"	"	"	3	7

* For the isomerization of butanes, $\Delta H_{12} = -8.1 \times 10^3$ kJ/kmol, $\Delta H_c = -57.3 \times 10^3$ kJ/kmol, $z_{10} = 0.99$, $z_{20} = 0.01$.

** For the isomerization of pentanes, $\Delta H_{12} = -7.9 \times 10^3$ kJ/kmol, $\Delta H_c = -57.3 \times 10^3$ kJ/kmol, $z_{10} = 0.99$, $z_{20} = 0.01$.

*** For the isomerization of hexanes, $\Delta H_{12} = -6.6 \times 10^3$ kJ/kmol, $\Delta H_{23} = -11.6 \times 10^3$ kJ/kmol, $\Delta H_c = -57.3 \times 10^3$ kJ/kmol, $z_{10} = 0.99$, $z_{20} = 0.01$, $z_{30} = 0$.

**** For the isomerization of xylenes, $\Delta H_{12} = -3 \times 10^3$ kJ/kmol, $\Delta H_{23} = -0.4 \times 10^3$ kJ/kmol, $\Delta H_c = -43.8 \times 10^3$ kJ/kmol, $z_{10} = 0.22$, $z_{20} = 0.50$, $z_{30} = 0.23$.

reaches 34-42 kelvins. Such an elevation of the temperature is not desirable and can detract from the selectivity of the main process. Therefore, the conducting of isomerization of *n*-butane or *n*-pentane in a single reactor is possible if the extent of the hydrocracking is limited to 1-2%.

The situation is the same for the isomerization of *n*-hexane with the formation of only methylpentanes. If, however, neohexane (or 2,3-dimethylbutane) also forms, the evolution of heat grows and may reach 27 °C even in the absence of hydrocracking. The involving of part of the feed stock in hydrocracking will increase the heating in the reactor still more. Consequently, in the isomerization of the pentane-hexane fraction with high conversions of the *n*-alkanes and the formation of considerable amounts of dimethylbutanes, it may be good to conduct the process in two consecutively arranged reactors with intermediate cooling of the reaction mixture.

In communications on the modification of the pentane-hexane fraction isomerization process, it is indicated that the reaction is carried on in two reactors [30]. This is consistent with the result of calculations we have performed and indicates that a catalyst making it possible to obtain a considerable amount of dimethylbutanes has been used.

The isomerization of xylenes proceeds with lower degrees of conversion than that of alkanes and with considerably lower heats of the reactions. This is why the magnitudes of ΔT_{ad} are insignificant. For reactions in the absence of hydrocracking, ΔT_{ad} can also be negative because one of the steps is endothermic.

In the hydrocracking of a part of the feed stock, the values of ΔT_{ad} grow, but remain relatively low. Therefore in the isomerization of xylenes without substantial hydrocracking, one should not fear major heating, and this process should be carried on in one reactor.

We shall give attention to two cases of employing formulas (5.39) and (5.40).

1. In specific calculations, the compositions of the mixtures can differ from those characterized in Table 23. This is associated with the processing in a number of cases of multicomponent mixtures such as a pentane-hexane fraction. Here formulas (5.39) and (5.40) should be used without any changes. It is only necessary to have in view that in schemes 1 and 2 the components A_1, A_2, and A_3 will be group ones. For example, in the processing of the pentane-hexane fraction, A_1 is the sum of *n*-pentane and *n*-hexane, A_2 is monomethyl-substituted C_5 and C_6, and A_3 is dimethyl-substituted C_5 and C_6.

The heats of the reactions change only slightly with a change in the molecular mass of the feed stock and remain the same (or are the average values) as in the calculations of individual substances.

2. In the technological processes, the feed stock may contain components not participating in isomerization, but subjected to reactions of cracking (hydrocracking). Let us designate their sum by B. For example, in many xylene isomerization processes, ethylbenzene does not practically participate in the formation of xylenes. In this case, we could also consider a more involved scheme than those given above, but the following approach will be simpler.

We first calculate ΔT_{ad} by formula (5.39) or (5.40) with no account of the reactions of components B. Next we find the correction $\Delta T'_{ad}$ according to the change in the mass of the components B, i.e. Δn_B, due to the reactions and to the heat of these reactions ΔH_B (the latter is easily determined by the methods of chemical thermodynamics):

$$\Delta T'_{ad} = \frac{\Delta H_B \Delta n_B}{GC_p}$$

The actual change in the temperature in this case is the sum of ΔT_{ad} and $\Delta T'_{ad}$.

The above calculations and their discussion show that the use of the formulas for calculating ΔT_{ad} substantially simplifies the determination of the heat regime at the outlet from a reactor in comparison with the traditional technological calculations performed according to the enthalpies of the reacting mixture components.

Using the above relations for ΔT_{ad}, it is also simple to calculate the heat of a process q_{pr}. Indeed, the total evolution of heat due to a process changes (raises) the reaction mixture temperature by ΔT_{ad}, therefore the heat of the process per unit mass of the feed stock (in kJ/kg) is:

$$q_{pr} = -\frac{GC_p \Delta T_{ad}}{G_0} = -\left[(1+\alpha)\left(\frac{1}{1+\alpha} C_{p,0} + \frac{\alpha}{1+\alpha} C_{p,g}\right)\right] \Delta T_{ad} \tag{5.41}$$

($q_{pr} < 0$ when heat is evolved).

Taking into account Eqs. (5.39) and (5.40) for ΔT_{ad}, we find: for scheme 1:

$$q_{pr} = -\frac{1}{M}\left[\left(\frac{1}{2}\Delta H_{12} + \Delta H_c\right)\Delta z_1 + \left(-\frac{1}{2}\Delta H_{12} + \Delta H_c\right)\Delta z_2\right] \tag{5.42}$$

for scheme 2:

$$q_{pr} = -\frac{1}{M}\left[\left(\frac{2}{3}\Delta H_{12} + \frac{1}{3}\Delta H_{23} + \Delta H_c\right)\Delta z_1 + \left(-\frac{1}{3}\Delta H_{12} + \frac{1}{3}\Delta H_{23} + \Delta H_c\right)\Delta z_2 + \left(-\frac{1}{3}\Delta H_{12} - \frac{2}{3}\Delta H_{23} + \Delta H_c\right)\Delta z_3\right] \tag{5.43}$$

Proceeding from the heats of isomerization and hydrocracking of individual hydrocarbons given in the footnotes to Table 23, we can propose the following simple expressions for calculating the heats of technical processes (in kJ per kilogramme of hydrocarbon being processed).

1. Isomerization of butanes:

$$q_{pr} = 1057\Delta z_1 + 918\Delta z_2 \tag{5.44}$$

2. Isomerization of pentanes:

$$q_{pr} = 851\Delta z_1 + 740\Delta z_2 \tag{5.45}$$

3. Isomerization of hexanes:

$$q_{pr} = 765\Delta z_1 + 688\Delta z_2 + 554\Delta z_3 \tag{5.46}$$

4. Isomerization of xylenes:

$$q_{pr} = 425\Delta z_1 + 397\Delta z_2 + 418\Delta z_3 \tag{5.47}$$

The heats of industrial isomerization processes conducted with a different degree of conversion have been calculated by Eqs. (5.44)-(5.47) and are given in Table 24. For purposes of illustration, we have

Table 24. **Heats of Isomerization Processes [Calculations by Formulas (5.44)-(5.47)]**

Content of hydrocarbons being isomerized in feed stock, mass fractions			Content of isomers in product, mass fractions			Change in isomer content, mass fractions			Heats of process, kJ/kg
A_1	A_2	A_3	z_1	z_2	z_3	Δz_1	Δz_2	Δz_3	
n-Butane	Isobutane	—	0.50	0.50	—	—0.49	0.49	—	—68*
$z_{10}=0.99$	$z_{20}=0.01$	—	0.50	0.48	—	—0.49	0.47	—	—87
			0.50	0.45	—	—0.49	0.44	—	—114
			0.60	0.40	—	—0.39	0.39	—	—54
n-Pentane	Isopen-	—	0.50	0.50	—	—0.49	0.49	—	—54**
$z_{10}=0.99$	tane	—	0.50	0.48	—	—0.49	0.47	—	—69
	$z_{20}=0.01$		0.50	0.45	—	—0.49	0.44	—	—91
			0.60	0.40	—	—0.39	0.39	—	—43
n-Hexane	Methyl-	Dimeth-	0.50	0.50	0	—0.49	0.49	0	—38***
$z_{10}=0.99$	pentanes	ylpen-	0.50	0.40	0.01	—0.49	0.39	0.01	—51
	$z_{20}=0.01$	tanes	0.50	0.49	0	—0.49	0.39	0	—106
		$z_{30}=0$	0.50	0.41	0.09	—0.49	0.40	0.09	—50
o-Xylene	*m*-Xylene	*p*-Xylene	0.30	0.35	0.30	0.08	—0.15	0.07	26****
$z_{10}=0.22$	$z_{20}=0.50$	$z_{30}=0.23$	0.35	0.25	0.35	0.13	—0.25	0.12	6
			0.35	0.24	0.35	0.13	—0.26	0.12	—5
			0.35	0.22	0.35	0.13	—0.28	0.12	—6

The calculations have been performed by formulas: *(5.44), **(5.45), ***(5.46), ****(5.47).

chosen the same regimes and compositions of the mixtures here as for Table 23.

It can be seen that the heats of the alkane isomerization processes are not great, but a noticeable growth in the evolution of heat is observed if a part of the feed stock is subjected to hydrocracking. In the conversions of xylenes, heat may either be absorbed or evolved, but the magnitudes of the heats are small.

5.2.2. Alkylation

The alkylation of reactant A by substance B can proceed as a multiple-step consecutive-parallel reaction:

$$\begin{array}{l} A \xrightarrow{+B} A_{11} \xrightarrow{+B} A_{12} \rightarrow \ldots \\ A \xrightarrow{+B} A_{12} \xrightarrow{+B} A_{22} \rightarrow \ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ A \xrightarrow{+B} A_{k1} \xrightarrow{+B} A_{k2} \rightarrow \ldots \end{array}$$

It is not difficult to calculate the heat of such a complex reaction from the enthalpies of formation of the reactants, but this is not convenient for analysis. If we take into account that the heats of steps of one type ($A \xrightarrow{+B} A_{i1} \xrightarrow{+B} A_{i2}$) are close in value, we can simplify the calculations substantially and obtain a simple equation for them. For example, the heats of alkylation of benzene and alkylbenzenes at 300-600 K are close to —102 kJ/mol of ethylene.

Assume that the heat of the i-th direction ($A_{ij} \xrightarrow{+B} A_{i,j+1}$) does not depend on j and has been related to one mole of B, i.e. $\Delta H_{i,B}$. Let $\Delta m_{i,B}$ be the number of moles of B that have reacted in the i-th direction. Hence the heat of the overall process calculated per $\sum_i \Delta m_{i,B}$ moles of B is

$$q_{pr} = \sum_i \Delta H_{i,B} \Delta m_{i,B}$$

If we may consider that the heats of all the directions are the same, i.e. $\Delta H_{i,B} = \Delta H_B$ and designate the overall consumption of substance B by $\sum_i \Delta m_{i,B} = \Delta m_B$, then the heat of alkylation is

$$q_{pr} = \Delta H_B \Delta m_B \qquad (5.48)$$

The quantity Δm_B can be determined from data on the composition of the liquid phase: $\Delta m_B = \sum_i j \mid \Delta m_{A_j} \mid$, where $j = 1$ for monoalkyl derivatives, $j = 2$ for dialkyl derivatives, and so on.

For example, the alkylation of benzene (A) using ethylene (B) with the formation of three diethylbenzenes (A_2), four triethylbenzenes (A_3), and ethylbenzene (A_1) can be characterized by a single reaction heat $\Delta H_{i,B} \approx \Delta H_B \approx \Delta H_B^\circ \approx -102$ kJ/mol of B. If only ethylbenzene is obtained in alkylation, we have $\Delta m_B = 1$ and $q_{pr} = -102$ kJ. If 0.5 mol of diethylbenzenes forms per mole of ethylbenzene, we have $\Delta m_B = 1 + 2 \times 0.5 = 2$, and $q_{pr} = -102 \times 2 = -204$ kJ. If the products contain 0.5 mol of diethylbenzenes and 0.25 mol of triethylbenzenes per mole of ethylbenzene, we have $\Delta m_B = 1 + 2 \times 0.5 + 3 \times 0.75 = 2.75$ and thus $q_{pr} = -102 \times 2.75 = -280.5$ kJ.

In the alkylation of isobutane using butenes at 300-400 K, we find that $\Delta H_{i,B} \approx \Delta H_B \approx \Delta H_B^\circ = -84$ kJ/mol of B. If only isooctane forms, we have $q_{pr} = -84 \times 1 = -84$ kJ, and when 0.2 mol of C_{12} hydrocarbons form per mole of isooctane, we find $\Delta m_B = 1 + 2 \times 0.2 = 1.4$, and $q_{pr} = -84 \times 1.4 = -117.6$ kJ.

In these examples, the heat being calculated has been related to Δm_B of consumed B. If it is necessary to determine the values of $\Delta H_{i,B}$ more precisely, we can use the generalized equations for ΔH_f° of hydrocarbons (see Appendix 1) or the values given in Appendix 2. It can be seen that the considered calculations are much simpler and illustrative than the direct use of the enthalpies of formation of the individual compounds.

5.2.3. Oxidation of Hydrocarbons by Oxygen

The oxidation of hydrocarbons by oxygen is employed for the industrial production of alcohols, acids, aldehydes and other compounds. It should be noted that no thermodynamic restrictions of conversion arise in these processes, and the methods of thermodynamics are used for heat calculations. The oxidation processes often have a low selectivity. They result in the preparation of a number of oxidation products such as alcohols, acids, aldehydes, ketones, ethers, esters, and peroxides. The oxidation products also contain certain amounts of CO_2, CO, H_2O, and H_2. It is significant that the number of carbon atoms in an initial molecule and the oxidation product may be different.

To calculate the heats of complex oxidation processes, we shall take advantage of the fact that the heats of reactions of one type do not depend on the molecular mass.

Assume that in a real process the reactant hydrocarbon R_1H with n_1 carbon atoms yields the following set of oxidation products: $R_{alc}OH$ (alcohol), $R_{ac}OOH$ (acid), R_aHO (aldehyde), R_oO (other products), CO_2, and CO. Let us consider two cases.

1. The number n of carbon atoms in the product and n_1 in the feed stock is the same. In this case, the calculations can be based on

the following hypothetic scheme:

$$RH + 0.5O_2 \xrightarrow{1} R_{alc}OH$$

$$RH + 1.5O_2 \xrightarrow{2} R_{ac}OOH + H_2O$$

$$RH + O_2 \xrightarrow{3} R_aHO + H_2O$$

$$RH + O_2 \xrightarrow{4} R_oO + H_2O$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$RH + \nu_1 O_2 \xrightarrow{c_1} nCO_2 + \nu_1' H_2O$$

$$RH + \nu_2 O_2 \xrightarrow{c_2} nCO_2 + \nu_2' H_2O + \nu_3' H_2$$

For heat calculations, the initial and final states of a system are important, the path followed in obtaining the products being of no significance. It is therefore of no importance whether the CO_2 forms in the individual steps (via the oxygen-containing derivatives) or directly from the carbon. Let us denote the amount of the products (in moles) obtained from one mole of the feed stock by a_{alc}, a_{ac}, a_a, a_o, $a(CO_2)$, $a(CO)$, and the heats of the steps in the above scheme by ΔH_1, ΔH_2, ΔH_3, ΔH_4, . . ., ΔH_{c_1}, and ΔH_{c_2}; all of them are related to one mole of the hydrocarbon. The heat of the process is therefore

$$q_{pr_1} = a_{alc}\Delta H_1 + a_{ac}\Delta H_2 + a_a\Delta H_3 + a_o\Delta H_4 + \ldots + \frac{a(CO_2)}{n}\Delta H_{c_1} + \frac{a(CO)}{n}\Delta H_{c_2}$$

or in the general form

$$q_{pr_1} = \sum a_i \Delta H_i + \frac{a(CO_2)}{n}\Delta H_{c_1} + \frac{a(CO)}{n}\Delta H_{c_2}$$

Here we have taken into consideration that the heats of steps 1-4... do not depend on the number of carbon atoms in the feed stock, while the heats of combustion (ΔH_{c_1} and ΔH_{c_2}) do depend on it. But if the heats of combustion are related to one mole of CO_2 ($\Delta H_{c_1}/n$) or CO ($\Delta H_{c_2}/n$), this dependence can be disregarded.

2. The number n of carbon atoms in the product and n_1 in the feed stock is different. We shall add to the scheme considered above a step that leads from a hydrocarbon with n_1 carbon atoms to one with n carbon atoms. It is not difficult to write the stoichiometric equation of this step if we know the decomposition products obtained in the real process. Thus, if the oxidate contains olefins (alkenes) (Ol), we can add to the scheme the cracking reaction $R_1H \rightarrow RH + Ol$ whose heat is ΔH_{cr}. It should be noted that the introduced step can be hypothetic, but actually formed products must participate in it.

Now, if one mole of the feed stock has been used and has yielded the same amounts of products as above, the heat of the process is

$$q_{pr_s} = q_{pr_1} + \Delta H_{cr} = a_{alc}\Delta H_1 + a_{ac}\Delta H_2 + a_2\Delta H_3 + a_0\Delta H_4 + \ldots + \frac{a(CO_2)}{n}\Delta H_{c_1} + \frac{a(CO)}{n}\Delta H_{c_2} + \Delta H_{cr}$$

The approach treated above shows the possibilities of calculating the heat of a complex technical process. It is more effective than calculations using the heats of formation of substances for a complex feed stock, for example, when oxidizing C_{10}-C_{20} alkanes to alcohols or C_{20}-C_{40} alkanes to acids.

Chapter 6

Thermodynamics of Mutual Hydrocarbon Conversion Reactions

In this chapter, we shall mainly deal with reactions of mutual hydrocarbon conversions not attended by the evolution or absorption of hydrogen, namely, without a change in the number of moles (isomerization, disproportionation), with a decrease in the number of moles (alkylation, polymerization), and with an increase in the number of moles (cracking and pyrolysis).

Thermodynamic calculations of simple gas-phase reactions of hydrocarbon conversion have been performed in the USSR by Tilicheev, Frost, Vvedensky, Obryadchikov, etc., and in other countries by Rossini, Egloff, Dodge, etc. References to these calculations are contained in [3, 4, 26, 31]. The expediency of a new consideration of the thermodynamics of these reactions is associated with the refinement of the previously obtained data, with the fact that for modern purposes these reactions have to be studied as complex ones and the calculations performed for both the gas and liquid phases, and also with the appearance of new branches such as the thermodynamics of complex reactions of isomerization, high-molecular polymerization, radical cracking, and pyrolysis.

Below, when considering the thermodynamics of specific reactions, we have used data both of investigations that have become classical, and of new investigations and calculations. The treatment of the thermodynamics of high-molecular polymerization has been combined with the analysis of a similar process, namely, high-molecular polycondensation. The section devoted to disproportionation includes data on the reactions of redistribution of hydrogen and carbon (the disproportionation of alkenes and coke formation).

In early investigations, the reliability of thermodynamic calculations was confirmed by comparing them with equilibrium experimental data.

At present, it is clear that the deviation of experimental data from calculated ones is associated not with the unreliability of the calculations, but only with the fact that some of the simple steps of a complex process have been left out of consideration. This is why only a small number of references are made to experimental studies.

6.1. Isomerization

The isomerization of C_4-C_{10} hydrocarbons is of the greatest technical significance, and the main attention is devoted to it below. The thermodynamic functions for the hydrocarbons used in the calculations are given in Appendix 2, and the working relations, in Secs. 1.2 and 1.3. It should be noted that isomerization reactions are often conducted at an increased pressure. How the pressure affects the heats, equilibrium constants, and degree of feed stock conversion is illustrated by Table 25.

The calculations have been performed with account taken of the non-ideal nature of the gaseous substances.

Examination of the data in Table 25 reveals that all the quantities change only slightly when the pressure is increased 150 times.

Isomerization reactions generally proceed with the formation of several products, and they cannot be described by a single stoichiometric equation. For example, *n*-pentane can form two isopentanes, *n*-1-butene can form three isomeric butenes. The ratio between the isomers in the course of a reaction changes, which excludes the possibility of their formation in one stage. It is absolutely natural to describe isomerization by a system of simple reactions each of which yields only one product. If A_2, A_3, and A_4 are the isomerization products of compound A_1, the following schemes of the process are possible, for example:

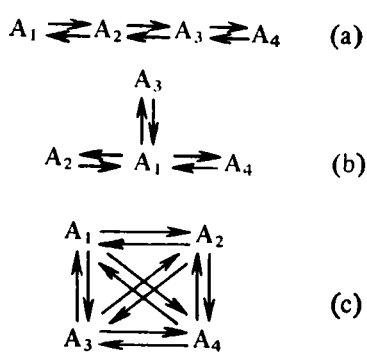


Table 25. **Data Characterizing the Effect of the Pressure on the Heats, Equilibrium Constants and Equilibrium Degrees of Conversion of Isomerization Reactions**

Reaction	Heat ΔH, kJ/mol				Equilibrium constant K_p°				Degree of feed stock conversion			
	300 K		700 K		300 K		700 K		300 K		700 K	
	0.1 MPa	15.0 MPa	0.1 MPa	15.0 MPa	0.1 MPa	15.0 MPa	0.1 MPa	15.0 MPa	0.1 MPa	15.0 MPa	0.1 MPa	15.0 MPa
n-Pentane → 2-methylbutane	—8.0	—7.8	—7.8	—7.5	13	13.2	2.1	2.2	0.93	0.94	0.68	0.69
o-Xylene → *p*-xylene	—1.0	—0.4	—2.8	—1.1	1.5	1.5	1.0	0.9	0.6	0.6	0.50	0.47
Cyclohexane → methylcyclopentane	—16.4	—15.0	—15.5	—14.2	5.1	5.1	0.1	0.1	0.84	0.84	0.1	0.1
1-Butene → isobutene	—16.8	—19.3	—16.2	—16.8	85.5	85.0	5.1	5.0	0.99	0.99	0.84	0.83

Which scheme is used is of no significance for calculating the composition of the equilibrium mixture because the path followed in achieving equilibrium does not matter in thermodynamic calculations. If a reaction follows scheme (a), but scheme (b) is used for calculating equilibrium, the final results of an experiment (after equilibrium has been reached) should coincide with the results of calculations. At the same time, it will be found in the course of a reaction that at a certain time the concentration of substance A_2 is higher than the equilibrium one. The only explanation is that the system has not yet reached complete equilibrium, but "partial" equilibrium during the real step $A_1 \rightleftarrows A_2$ has been achieved. We shall treat this matter in greater detail on a following page.

We shall note, however, that for calculating equilibrium in a system with m reactants, it is sufficient to know the equilibrium constants of $m - 1$ reactions. Even if a larger number of reactions proceed in a real system, there is no need to find the equilibrium constants for all these reactions. For example, calculations by scheme (c) with six reactions result in the same composition as calculations by scheme (a) with three reactions. The explanation is that only $(m - 1)$ reactions and $(m - 1)$ equilibrium constants are independent.

For this reason, linear schemes of type (a) or "wye" schemes of type (b) are convenient for calculating the equilibrium compositions, because for them m substances participate in $m - 1$ reactions.

It is easy to determine the equilibrium constants K_{ij} of each simple step from the thermodynamic functions of the reaction mixture components. Here we shall consider the determination of the amounts of the components in an equilibrium mixture from the known values of K_{ij} of the simple steps.

1. *For a linear scheme.* Assume that the scheme of isomerization reactions in the gas phase is as follows:

$$A_1 \underset{}{\overset{K_{p12}}{\rightleftarrows}} A_2 \ldots \overset{K_{pj-1,j}}{\rightleftarrows} A_j \overset{K_{pj,j+1}}{\rightleftarrows} \ldots \overset{K_{pm-1,m}}{\rightleftarrows} A_m \qquad \text{(XII)}$$

The equilibrium mixture contains m isomers. If the mixture's composition is characterized by their equilibrium partial pressures p_j, we obtain $m - 1$ equations for the independent equilibrium constants:

$$\left.\begin{aligned} K_{p,12} &= \frac{p_2}{p_1} \\ &\ldots\ldots\ldots \\ K_{p,j-1,j} &= \frac{p_j}{p_{j-1}} \\ &\ldots\ldots\ldots \\ K_{p,m-1,m} &= \frac{p_m}{p_{m-1}} \end{aligned}\right\} \qquad (6.1)$$

To determine m unknown values of p_j, we need another equation. We can write it by having in view that the total pressure p in the system does not change:

$$\sum_{j=1}^{m} p_j = p \tag{6.2}$$

It follows from (6.1) that

$$p_2 = K_{p,12}p_1, \quad p_3 = K_{p,23}p_2 = K_{p,12}K_{p,23}p_1$$

And in general, for any value of p_j, we have

$$p_j = p_1 \prod_{i=2}^{j} K_{p,i-1,i} \tag{6.3}$$

Here

$$\prod_{i=2}^{j} K_{p,i-1,i} = K_{p,12}K_{p,23} \ldots K_{p\ j-1,j}$$

Introducing (6.3) into (6.1) and knowing that $p_1 + \sum_{j=2}^{m} p_j = p$, we find

$$p_1 = \frac{1}{1+\sum_{j=2}^{m}\prod_{i=2}^{j} K_{p,i-1,i}}\,p, \quad p_j = \frac{\prod_{i=2}^{j} K_{p,i-1,i}}{1+\sum_{j=2}^{m}\prod_{i=2}^{j} K_{p,i-1,i}}\,p \tag{6.4}$$

If we employ the mole fractions of the components in the equilibrium mixture ($x_j = p_j/p$) to characterize the equilibrium composition, we obtain by (6.4):

$$x_1 = \frac{1}{1+\sum_{j=2}^{m}\prod_{i=2}^{j} K_{p,i-1,i}}, \quad x_j = \frac{\prod_{i=2}^{j} K_{p,i-1,i}}{1+\sum_{j=2}^{m}\prod_{i=2}^{j} K_{p,i-1,i}} \tag{6.5}$$

For example, using relations (6.5) for scheme (a), we find x_2:

$$x_2 = \frac{K_{p,12}}{1+K_{p,12}+K_{p,12}K_{p,23}+K_{p,12}K_{p,23}K_{p,34}}$$

2. *For a "wye" scheme.* It is easy to see that

$$\prod_{i=2}^{j} K_{p,i-1,i} = K_{p,1j} \tag{6.6}$$

Indeed, for example,

$$\prod_{i=2}^{4} K_{p,i-1,i} = K_{p,12}K_{p,23}K_{p,34} = \frac{p_2}{p_1}\,\frac{p_3}{p_2}\,\frac{p_4}{p_3} = \frac{p_4}{p_1} = K_{p,14}$$

Consequently, relations of the type of (6.4) and (6.5) for calculations of p_j and x_j are simplified if we calculate equilibrium not for the linear scheme (a), but for wye scheme (b). For the latter, from (6.4) and (6.5) with a view to (6.6), we obtain:

$$p_j = \frac{K_{p,1jp}}{1+\sum\limits_{j=2}^{m} K_{p,1,j-1}} = \frac{K_{p,1jp}}{\sum\limits_{j=1}^{m} K_{p,1j}}; \quad K_{p,11} = 1 \tag{6.7}$$

$$x_j = \frac{K_{p,1j}}{1+\sum\limits_{j=2}^{m} K_{p,1j}} = \frac{K_{p,1j}}{\sum\limits_{j=1}^{m} K_{p,1j}}; \quad K_{p,11} = 1 \tag{6.8}$$

The equilibrium compositions can be calculated for schemes (a) and (b) by (6.4) and (6.5) or by (6.7) aad (6.8), for example

$$x_2 = \frac{K_{p,12}}{1+K_{p,12}+K_{p,13}+K_{p,14}}$$

If isomerization is conducted in the liquid phase, the above method of calculations must be supplemented with an analysis of the equilibrium between the liquid and gas phases.

The working formulas relating the composition of the gas and liquid phases are given in Sec. 2.4. The following of them can be used:

$$x_{j,\mathrm{lq}} = \frac{x_j/p_j^\circ}{\sum\limits_{j=1}^{m} x_j/p_j^\circ} = \frac{K_{p,1j}/p_j^\circ}{\sum\limits_{j=1}^{m} K_{p,1j}/p_j^\circ}; \quad K_{p,11} = 1 \tag{6.9}$$

For illustration, Table 26 compares the equilibrium compositions for selected simple and complex isomerization reactions in the gas and liquid phases [it is assumed that the ideal gas laws and expressions (6.1)-(6.8) hold for the gas phase].

It can be seen from the data of Table 26 that the compositions of the equilibrium gas and liquid phases differ more when the difference between the saturated vapour pressures of the pure components is greater. For example, in the isomerization of pentanes at 300 K, the content of 2-methylbutane in the gas phase is 44%, and in the liquid phase, 57%. With elevation of the temperature, the compositions of the equilibrium gas and liquid phases generally approach each other.

Analysis of relations (6.9) and the data of Table 26 reveals that isomerization in the liquid phase can be more profitable thermodynamically if it is desired to produce an isomer with a low saturated vapour pressure and a high boiling point.

Table 26. **Equilibrium Compositions for Selected Isomerization Reactions in the Gas and Liquid Phases**

Hydrocarbon	Saturated vapour pressure p_j°, MPa × 10^{-1}		Content, fractions			
			in equilibrium gas phase		in equilibrium liquid phase	
	300 K	400 K	300 K	400 K	300 K	400 K
n-Pentane	0.68	10.3	0.03	0.11	0.05	0.14
2-Methylbutane	0.92	12.2	0.44	0.65	0.57	0.69
2,2-Dimethylpropane	1.70	18.6	0.53	0.24	0.38	0.17
o-Xylene	0.009	0.62	0.16	0.19	0.17	0.22
p-Xylene	0.01	0.74	0.60	0.57	0.59	0.55
m-Xylene	0.01	0.72	0.24	0.24	0.24	0.23
Methylcyclopentane	0.18	4.2	0.12	0.38	0.09	0.43
Cyclohexane	0.13	3.4	0.88	0.62	0.91	0.57
1-Butene	3.0	29.4	0.01	0.05	0.01	0.05
Isobutene	3.0	29.8	0.99	0.95	0.99	0.95

6.1.1. Some Problems in the Experimental Determination of the Equilibrium Mixture Composition in Isomerization

For a large number of hydrocarbons with nine or more carbon atoms, the thermodynamic functions are not determined, but are calculated by approximate methods. Therefore, experimental studies for verifying the calculated equilibrium compositions are quite natural. Moreover, for hydrocarbons with nine or more carbon atoms, owing to the large number of isomers possible, of interest are "partial" equilibria of only those isomers that form in the reaction system in appreciable amounts. This is why the experimental determination of the equilibrium composition of isomer hydrocarbons remains an important method for studying isomer conversions. A review of a number of works involving the experimental determination of equilibrium hydrocarbon compositions is contained in the sections devoted to the isomerization of alkanes, cycloalkanes, aromatics, and alkenes. We can note the experimental studies of the equilibrium of alkanes and cycloalkanes performed by Petrov and his collaborators [32, 33].

The unchanging proportion of the isomers with different substantial durations of conducting a reaction or the same proportion of the isomers for several different feed stock mixtures is usually considered to be a proof of the achievement of equilibrium in experimental studies. Frequently, experimental investigations do indeed characterize the equilibrium composition, but on-

ly when isomerization is not attended by irreversible side reactions (such as cracking or hydrogenolysis), or by the binding of appreciable amounts of the hydrocarbons into a complex with a catalyst. In the indicated cases, the unchanging composition of the reaction mixture at different durations of contact or for different feed stock compositions does not signify that the proportion of the isomers is the same as in thermodynamic equilibrium. Below we shall treat in greater detail the causes of the possible deviations of the experimental compositions from the "true" thermodynamically equilibrium ones.

When irreversible side reactions proceed, the difference between the experimental and "true" equilibrium compositions can be proved analytically. Let us consider the simplest system of reactions for this purpose:

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} A_2 \qquad A_1 \xrightarrow{k_1} B \qquad A_2 \xrightarrow{k_2} B$$

where A_1 and A_2 are isomers, B is a side product, and k is the rate constant. Let all the reactions be first-order ones with respect to the reactant. Now the change in the concentrations c of substances A_1 and A_2 with the time τ is described by the following system of equations (it is assumed that the process occurs in a static system):

$$\frac{dc_1}{d\tau} = k_{21}c_2 - (k_{12} + k_1)\,c_1; \qquad \frac{dc_2}{d\tau} = -(k_{21} + k_2)\,c_2 + k_{12}c_1$$

Integration of the above system results in the following ratio of the concentrations of the isomers A_1 and A_2 at large values of τ:

$$\frac{c_2}{c_1} = \frac{K}{2}\left[\delta + \left(\delta^2 + \frac{4}{K}\right)^{1/2}\right] \tag{6.10}$$

where K is the equilibrium constant, and $\delta = 1 - (1/K) - [(k_1 - k_2)\,k_{12}]$. It is obvious that the ratio c_2/c_1 can differ from K at a long duration of the reaction. Below are given some values of c_2/c_1 for various sets of rate constants that have been calculated by Eq. (6.10).

k_{12}	k_1	k_2	k_2	$\left(\frac{c_2}{c_1}\right)_{\tau\to\infty}$	$K = \frac{k_{12}}{k_{21}}$	$\left(\frac{c_2}{c_1}\right)_{\tau\to\infty}$	K
1	0.01	0.1	0.01	10	10	1	
1	0.01	1	0.01	1	1	1	
1	0.01	0.1	0.001	10.5	10.0	1.05	
0.01	0.01	0.001	0.001	18.5	10.0	1.85	
0.01	0.1	0.001	0.001	110	10.0	11	
0.01	0	0.01	0.001	0.95	1	0.95	

A glance at the above data reveals that when the rates of the side reactions are appreciable (in comparison with the rates of isomerization), the observed (experimental) and equilibrium ratios of the iso-

mers can differ noticeably, and c_2/c_1 can be either larger or smaller than the equilibrium constant. It is difficult to employ Eq. (6.10) for analysing real situations because the rate constant changes in the course of a reaction owing to disactivation. But it is obvious that equilibrium can be studied experimentally only in the absence of or at very low rates of the side reactions.

With a view to the above, in the experimental determination of the equilibrium composition, one should give preference to the use of catalysts such that do not activate cracking or hydrogenolysis, for example, to aluminium chlorides or bromides, or boron fluoride. Promoters such as HCl, HF, HBr, and H_2 are added to these catalysts to increase their activity.

If the amount of the catalyst is considerable, however, a new complex of the reactants and catalyst can form. For example, a solution of boron fluoride in anhydrous hydrogen fluoride used as a xylene isomerization catalyst forms stable complexes with xylenes dissoluble in the acid. It was established that the complex of *m*-xylene is more stable than those of the other xylenes [34]. With this in view, by using a large excess of the catalyst (three moles of boron fluoride and six moles of hydrogen fluoride per mole of xylenes), one can completely isomerize *p*-xylene to *m*-xylene at 30 °C, although the equilibrium content of the latter is below 70%. This example shows the possibility of substantial errors in the experimental determination of equilibrium compositions and, from them, the equilibrium constants.

It is clear from the above that such a determination is permissible when catalysts are used that have a very high selectivity with respect to isomerization in small concentrations.

Measurements of the equilibrium composition and the experimental equilibrium constants can be used to determine $\Delta H°$ and $\Delta S°$ and compare their values with those found from thermochemical measurements. Thus, it follows from the equation of an isobar that the slope of a straight line in the coordinates $\ln K_{p,T}$ versus $1/T$ equals $\Delta H°/R$. If the equilibrium constants have been measured only at two temperatures, $\Delta H°$ is calculated by the following equation:

$$\Delta H° = R \ln \frac{K_{p,T_2}}{K_{p,T_1}} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \qquad (6.11)$$

Next from the values of $K^{\ominus}_{p,T_1}$ and $\Delta H°$, it is easy to determine $\Delta S°$ by the equation of an isotherm

$$-\Delta H° + T_1 \Delta S° = RT_1 \ln K_{p,T_1} \qquad (6.12)$$

Table 27 on the basis of results given in [34] compares the values of $\Delta H°$ and $\Delta S°$ determined from the data of standard thermodynamic tables and from experimentally measured equilibrium constants for the gas-phase isomerization of alkanes and aromatics.

Table 27. **Data on $\Delta H°$ and $\Delta S°$ for the Gas-Phase Isomerization of Alkanes and Aromatics**

Reaction	Heat of isomerization $\Delta H°$, J/mol		Change in entropy in isomerization $\Delta S°$, J/(mol·K)	
	from standard thermodynamic tables	from measurements	from standard thermodynamic tables	from measurements
n-C_4H_{10} → iso-C_4H_{10}	8580	9700	15	18
n-C_5H_{12} → iso-C_5H_{12}	8075	7790	5.6	5.4
n-C_6H_{14} → 2-methylpentane	7280	7030	7.6	7.7
n-C_6H_{14} → 3-methylpentane	4400	4560	8.4	7.1
n-C_6H_{14} → 2,2-dimethylbutane	17 990	20 710	28.8	41.8
n-C_6H_{14} → 2,3-dimethylbutane	10 670	10 460	22.9	25.9
m-Xylene → p-xylene	670	1920	—	—
m-Xylene → o-xylene	1880	3970	—	—

Examination of Table 27 shows that in all cases the values found from standard thermodynamic tables, i.e. from calorimetric measurements, and on the basis of the experimental measurement of the equilibrium constants differ. Although the magnitudes of the deviations are not large [approximately up to 2 kJ/mol in the heats and up to 10 J/(mol·K) in the changes in the entropy], their relative values may reach 100% of $\Delta H°$ or $\Delta S°$. The above data show the prudency of verifying the values of the thermodynamic functions in different ways.

Naturally, the compositions calculated from the thermodynamic functions and the experimental equilibrium compositions will also fail to coincide exactly (Table 28).

The data of Table 28 show the "extreme" situation, when the discrepancies between the experimental and calculated values are high.

Table 28. **Experimental and Calculated Compositions of Equilibrium Mixture of Heptanes at 293 K [34]**

Hydrocarbon	Content in equilibrium mixture, %	
	calculated	experimental
n-Heptane	2.2	10
2-Methylhexane	15.7	21.8
3-Methylhexane	8.6	11.7
2,3-Dimethylpentane	44.6	13.3
2,4-Dimethylpentane	17.7	28.6
2,2,3-Trimethylbutane	11.2	15.0

For example, the experimentally obtained content of 2,3-dimethylpentane is practically one-fourth of the calculated value. Here we cannot naturally consider that the experimental data characterize true equilibrium. It is much more probable that for the reasons indicated above, equilibrium was not reached in the experiment. Consequently, a different catalyst must be used for studying it experimentally. But with an active catalyst too, because of kinetic difficulties, the rates of formation of some isomers can be so low that an experiment yields not complete equilibrium between all the possible isomers, but only partial equilibrium between some of them formed or consumed at a significant rate. We can easily see that for the above data, equilibrium sets in between the monomethyl-substituted compounds, but not between the dimethyl-substituted ones.

There are many examples, however, given below, when the coincidence of the calculated and experimental compositions of isomer mixtures is quite satisfactory.

6.1.2. Alkanes

Thermodynamic Parameters of Isomerization. Table 29 gives the heats, changes in the entropy, and the equilibrium constants for alkane isomerization reactions in the gas phase.

Inspection of the data in Table 29 reveals that for reactions of one type ΔH° and ΔS° are close in value. Here if we do observe cases of an appreciable deviation of the values of one of the quantities (ΔH°, ΔS°) from the mean one for alkanes with four to six carbon atoms, then for *n*-heptane to *n*-decane the scatter of the values of ΔH° and ΔS° is considerably lower. For example, for *n*-heptane to *n*-decane, the heat of the reaction of isomerization to a 2-methyl-substituted alkane at 300 K fluctuates from 7.1 to 7.2 kJ/mol, and the change in the entropy varies from 7.9 to 11.5 J/(mol·K). When 2,2-dimethyl-substituted isomers are obtained at 300 K, the value of ΔH° ranges from 16.3 to 18.3 kJ/mol, and that of ΔS° from 32.5 to 35.5 J/(mol·K).

One must have in view that the data on the heats of formation and entropies of alkanes with seven and more carbon atoms are not always accurate. These data obtained from different sources can differ by 10-20%. It should be noted that a similar failure of the heat of a reaction and the entropy change to depend on the molecular mass of the feed stock was also observed previously [30, 34]. This allows us not to consider separately the equilibrium compositions for each alkane with seven or more carbon atoms, but to characterize this equilibrium by the total composition, indicating the content of the normal alkane, the 2-methyl-substituted, 3-methyl-substituted ones, etc. The relevant equilibrium constants $\overline{K}_{p,ij}$ can be evaluated from the mean heats $\overline{\Delta H}^\circ_{ij}$ and entropy changes $\overline{\Delta S}^\circ_{ij}$ for reactions of

Table 29. **Heats $\Delta H°$ (in kJ/mol), Changes in Entropy $\Delta S°$ [in J/(mol·K)], and Equilibrium Constants K_p for Normal Alkane Isomerization Reactions in the Gas Phase**

Reaction	Thermodynamic quantities at T, K								
	300			500			700		
	$-\Delta H°$	$-\Delta S°$	K_p	$-\Delta H°$	$-\Delta S°$	K_p	$-\Delta H°$	$-\Delta S°$	K_p
n-Butane → 2-Methylpropane	8.4	15.5	4.5	8.2	15.3	1.2	8.0	14.8	0.7
n-Pentane → 2-Methylbutane	8.0	5.4	13	8.1	4.5	3.6	7.8	5.2	2.1
n-Hexane → 2-Methylpentane	7.1	7.9	6.7	6.6	6.8	2.2	6.1	5.9	1.4
n-Heptane → 2-Methylhexane	7.2	7.9	6.8	7.2	7.9	2.2	7.1	7.9	1.3
n-Octane → 2-Methylheptane	7.1	11.5	4.2	7.0	11.5	1.4	7.0	11.5	0.8
n-Decane → 2-Methylnonane	7.1	10.1	5.2	6.1	7.3	1.8	5.4	16.2	1.2
Mean values*	7.1	9.8	5.3	6.8	8.9	1.7	6.2	11.2	0.8
n-Hexane → 3-Methylpentane	4.4	8.6	2.1	4.3	8.6	1.03	4.4	8.6	0.8
n-Heptane → 3-Methylhexane	4.5	3.8	3.9	4.1	3.8	1.9	4.5	3.8	1.4
n-Octane → 3-Methylheptane	4.2	5.1	2.9	3.3	5.1	1.5	4.2	5.1	1.1
n-Decane → 3-Methylnonane	4.3	4.3	3.3	3.8	3.0	1.7	3.3	2.2	1.4
Mean values*	4.3	4.4	3.3	3.7	4.3	1.5	3.0	3.7	1.0
n-Hexane → 2,3-Dimethylbutane	10.6	22.7	4.6	10.7	23.2	1.0	10.5	22.9	0.4
n-Heptane → 2,3-Dimethylpentane	11.5	13.8	18.7	11.4	13.8	1.5	9.3	13.8	1.4
n-Decane → 2,3-Dimethyloctane	11.5	17.4	12.2	11.5	17.8	1.9	11.2	17.3	0.9
Mean values*	11.5	15.6	15.1	11.5	15.8	1.8	10.2	15.6	0.9
n-Pentane → 2,2-Dimethylpropane	19.5	42.5	15	18.7	40.5	0.69	17.4	38.3	0.2

Table 29 (*concluded*)

Reaction	Thermodynamic quantities at T, K								
	300			500			700		
	$-\Delta H°$	$-\Delta S°$	K_p	$-\Delta H°$	$-\Delta S°$	K_p	$-\Delta H°$	$-\Delta S°$	K_p
n-Hexane → 2,2-Dimethylbutane	18.3	30.1	14.5	18.2	29.8	2.2	17.4	28.5	0.6
n-Heptane → 2,2-Dimethylpentane	18.3	34.9	13.7	18.3	34.9	1.2	18.3	34.9	0.3
n-Octane → 2,2-Dimethylhexane	16.3	35.5	9.5	16.3	35.5	0.7	16.3	35.5	0.2
n-Decane → 2,2-Dimethyloctane	17.8	32.9	24	16.0	28.3	1.5	14.1	25.2	0.5
Mean values*	17.5	34.4	17.8	16.9	32.9	1.1	16.2	31.6	0.5
n-Heptane → 2,4-Dimethylpentane	14.2	31.2	8.4	14.2	31.2	0.7	14.2	31.2	0.3
n-Octane → 2,4-Dimethylhexane	11.0	21.1	8.1	11.0	21.1	1.1	11.0	21.1	0.5
n-Nonane → 2,4-Dimethylheptane	11.5	17.1	11.8	12.0	18.2	1.9	11.6	17.8	0.9
Mean values*	12.2	23.1	8.1	12.4	24.4	1.0	12.3	23.4	0.4
n-Heptane → 3-Ethylpentane	1.9	16.4	0.3	1.9	16.4	0.22	1.9	16.4	0.2
n-Octane → 3-Ethylhexane	2.4	8.5	0.9	2.4	8.5	0.65	2.4	8.5	0.08
n-Nonane → 3-Ethylheptane	1.4	9.8	0.5	1.7	10.5	0.42	1.5	10.2	0.4
Mean values*	1.9	11.6	0.5	2.0	12.8	0.36	2.3	11.7	0.4
n-Octane → 2,2,4-Trimethylpentane	15.7	43.5	1.1	15.7	43.5	0.23	15.7	43.5	0.08
n-Nonane → 2,2,4-Trimethylhexane	14.2	39.8	2.5	13.9	39.3	0.25	12.4	36.7	0.1
n-Decane → 2,2,4-Trimethylheptane	14.2	40.2	2.4	13.6	38.9	0.24	12.6	36.2	0.1
Mean values*	14.7	41.2	2.5	14.4	40.6	0.24	13.1	38.8	0.09

* The mean values of the above quantities are given for reactions of C_7-C_{10} alkanes; they have been determined from data on a larger number of reactions than are given in Table 29.

one type:

$$\ln \overline{K}_{p,ij} = -\frac{\overline{\Delta H}^{\circ}_{ij} - T\overline{\Delta S}^{\circ}_{ij}}{RT} \qquad (6.13)$$

The mean values $\overline{\Delta H}^{\circ}_{ij}$, $\overline{\Delta S}^{\circ}_{ij}$, and $\overline{K}_{p,ij}$ are also given in Table 29.

Let us treat the results obtained in greater detail.

We shall note some general laws for the heats of isomerization of alkanes.

1. The isomerization of *n*-alkanes proceeds with a small evolution of heat. When isomers of various structures form from *n*-alkanes, the heat of the reaction ranges from —2 to —20 kJ/mol, which is below, for example, the heat of condensation of *n*-hexane (—28.9 kJ/mol).

2. The heats of isomerization change only slightly with the temperature. When the temperature is increased by 400 K, the heat of a reaction either diminishes insignificantly in magnitude or remains unchanged.

3. The heat of isomerization of an *n*-alkane is determined not by the number of substituents in the side chain, but only by their mutual arrangement. Thus, in the formation of a 2-methyl-substituted isomer, the heat of the reaction (in magnitude) is almost double that in the formation of a 3-methyl-substituted one. The heat of formation of a 2,2-dimethyl-substituted isomer is somewhat higher than that of a 2,2,4-trimethyl-substituted one. Attention is deserved by the low (in magnitude) heat of transition of an *n*-alkane to a 3-methyl-substituted isomer.

As regards the equilibrium constants, they are characterized by the following.

1. With elevation of the temperature, all the equilibrium constants of *n*-alkane $\rightarrow$ isomer reactions decrease, i.e. low temperatures are favourable for the isomerization of normal alkanes.

2. When comparing the equilibrium constants of formation of various isomers from *n*-alkanes, we can see that at low temperatures (300 K) the formation of 2,2-, 2,3-, and 2,4-dimethyl-substituted isomers is more probable thermodynamically, and then of 2-methyl- and 3-methyl-substituted ones. Ethyl- and trimethyl-substituted isomers can form in relatively small amounts.

At high temperatures (700 K), the equilibrium constants of various reactions approach one another, and the formation of 2-methyl-, 3-methyl-, and 2,3-dimethyl-substituted isomers becomes more probable thermodynamically.

Equilibrium Compositions in Isomerization. Let us now consider data on the equilibrium compositions of isomerization products. The values of K_p given in Table 29 enable us to calculate these compositions by using the "wye" scheme and expressions (6.4)-(6.8). In accordance with what has been said above, we can consider the

equilibrium compositions separately: (a) for butanes, (b) for pentanes, (c) for hexanes, and (d) for alkanes with seven and more carbon atoms.

We must also take into consideration that all the isomers rarely form in real processes. Consequently, for comparing the thermodynamically equilibrium composition with an experimental one, we should use data on the equilibrium of only the isomers that are present in the reaction products in noticeable amounts. If, for example, methylbutane forms in the isomerization of *n*-pentane, the equilibrium between these two alkanes must be considered, but not between the three existing pentane isomers. Unfortunately, this circumstance is not always held in mind by experimenters, and this results in incorrect conclusions on the apparent disturbance of thermodynamic equilibrium (for greater detail, see [30]). With a view to the above, in the following we give data both on the total equilibrium mixtures (all possible isomers) and on partial equilibrium mixtures (with a limited number of isomers formed in real processes (see Tables 30-35 and Figs. 15-18). These tables are intended for use in experimental and theoretical research; the data contained in them are helpful when analysing a large number of real situations.

At the same time, if information is needed on the equilibrium compositions of other mixtures or for other temperatures, it is good to employ the following considerations. If a real mixture contains only a part of the isomers characterized in Tables 30-35, the ratio between them will be the same as in the more complicated mixtures. Thus, if only structures III and IV form from *n*-hexane (see Table 31) the ratio between III and IV, for example, at 700 K, will be the same as in Table 31 (i.e. 1.31). Knowing the ratios between the amounts of the isomers x_i/x_j and using the condition that the sum of the fractions of the components equals unity, we can find the content of each component.

Table 30. **Equilibrium Compositions of Butane and Pentane Isomerization Products (Fractions)**

Alkane	Temperature, K	*n*-Alkane (I)	2-Methyl-substituted (II)	2,2-Dimethyl-substituted (III)
Butane	300	0.18	0.82	—
	500	0.45	0.55	
	700	0.59	0.41	
Pentane with formation of I and II	300	0.07	0.93	—
	500	0.22	0.78	
	700	0.32	0.68	—
Ditto, I, II, and III	300	0.03	0.45	0.52
	500	0.19	0.68	0.13
	700	0.30	0.64	0.06

When estimating the equilibrium compositions for temperatures from 300 to 700 K, we can employ interpolation of the data of Tables 30-35 and Figs. 15-18. If accurate data on the equilibrium compositions are required or the temperature an investigator is interested in is outside the interval 300-700 K, one should calculate the

Table 31. **Equilibrium Compositions of Hexane Isomerization Products (Fractions)**

Equilibrium mixture of substances	Temperature, K	*n*-Alkane (I)	2-Methyl-substituted (II)	3-Methyl-substituted (III)	2,2-Dimethyl-substituted (IV)	2,3-Dimethyl-substituted (V)
I and II	300	0.13	0.87	—	—	—
	500	0.31	0.69	—	—	—
	700	0.42	0.58	—	—	—
I, II and III	300	0.10	0.69	0.21	—	—
	500	0.24	0.52	0.24	—	—
	700	0.31	0.44	0.25	—	—
I-IV	300	0.04	0.28	0.09	0.59	—
	500	0.16	0.34	0.16	0.34	—
	700	0.26	0.37	0.21	0.16	—
I-V	300	0.03	0.23	0.07	0.51	0.16
	500	0.14	0.29	0.14	0.29	0.14
	700	0.24	0.33	0.19	0.15	0.09

Table 32. **Equilibrium Compositions of Isomerization Products of C_7 and Higher Alkanes (Fractions)**

Equilibrium mixture of substances	Temperature, K	*n*-Alkane (I)	2-Methyl-subst. (II)	3-Methyl-subst. (III)	2,2-Dimethylsubst. (IV)	2,3-Dimethylsubst. (V)	2,4-Dimethylsubst. (VI)	3-Ethyl-subst. (VII)	2,2,4-Trimethylsubst. (VIII)*
I and II	300	0.16	0.84	—	—	—	—	—	—
	500	0.37	0.63	—	—	—	—	—	—
	700	0.56	0.44	—	—	—	—	—	—
I, II, and III	300	0.10	0.55	0.35	—	—	—	—	—
	500	0.24	0.40	0.36	—	—	—	—	—
	700	0.36	0.28	0.36	—	—	—	—	—
I-VII	300	0.02	0.10	0.06	0.35	0.30	0.16	0.01	—
	500	0.12	0.20	0.18	0.13	0.20	0.25	0.02	—
	700	0.20	0.16	0.20	0.10	0.18	0.08	0.08	—
I-VIII	300	0.02	0.10	0.06	0.33	0.28	0.15	0.01	0.05
	500	0.11	0.20	0.17	0.13	0.20	0.11	0.05	0.03
	700	0.19	0.16	0.20	0.10	0.18	0.08	0.08	0.01

* Data for C_8 and higher alkanes.

Table 33. **Equilibrium Constants of Isomerization of *n*-Alkanes to Monomethyl-Substituted Isomers with a Different Position of the Methyl Group**

Isomer	Number of carbon atoms	Isomerization equilibrium constants at temperature, K		
		300	500	700
2-Methylalkane	8	4.2	1.4	0.9
	9	5.4	1.8	1.2
	10	5.3	1.7	0.8
3-Methylalkane	8	2.8	1.5	1.1
	9	3.5	1.8	1.3
	10	3.3	1.5	1.0
4-Methylalkane	8	0.8-0.9	0.5	0.4
	9	3.5	1.8	1.3
	10	3.3	1.4	1.3
5-Methylalkane	10	1.7	0.9	0.7

Table 34. **Data on the Experimental (e) and Calculated (c) Content of Methylalkanes in Their Equilibrium Mixture at 700 K**

Isomer	Content (in %) in isomerization									
	n-$C_{12}H_{26}$		n-$C_{13}H_{28}$		n-$C_{14}H_{30}$		n-$C_{15}H_{32}$		n-$C_{16}H_{34}$	
	e	c	e	c	e	c	e	c	e	c
2-Methylalkane	25	22	22	20	19	18	18	17	15	16
3-Methylalkane	28	22	23	20	22	18	21	17	20	15
4-Methylalkane	19	22	19	20	17	18	17	17	14	15
5-Methylalkane	20	22	19	20	19	18	17	17	15	15
6-Methylalkane	9	12	17	20	15	18	14	16	14	15
7-Methylalkane	—	—	—	—	8	10	13	16	14	15
8-Methylalkane	—	—	—	—	—	—	—	—	8	9

Table 35. **Equilibrium Compositions of Isomerization Products of Alkyl-Substituted C_7 and Higher Alkanes (Fractions)**

Equilibrium mixture of substances	Temperature, K	2-Methyl-substituted (I)	3-Methyl-substituted (II)	3-Ethyl-substituted (III)	2,3-Dimethyl-substituted (IV)
I and II	300	0.63	0.37	—	—
	500	0.53	0.47	—	—
	700	0.38	0.62	—	—
III and IV	300	—	—	0.03	0.97
	500	—	—	0.20	0.80
	700	—	—	0.31	0.69

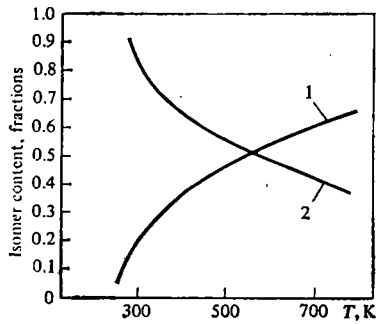


Fig. 15. Composition of equilibrium mixtures of two alkane isomers (for C_7 and higher alkanes):
1—normal, *2*—methyl-substituted

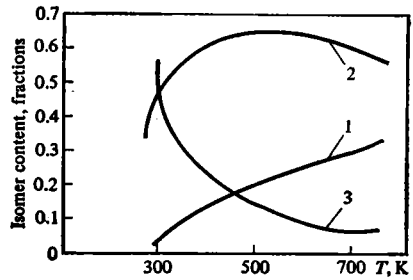


Fig. 16. Composition of equilibrium mixtures of three alkane isomers (for C_7 and higher alkanes):
1—normal; *2*—2-methyl-substituted; *3*—2,2-dimethyl-substituted

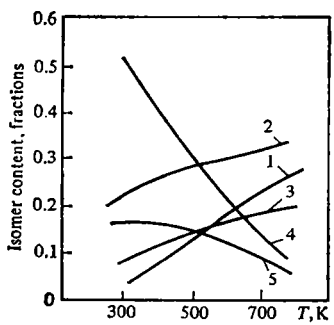


Fig. 17. Composition of equilibrium mixtures of five alkane isomers (for C_7 and higher alkanes):
1—normal; *2*—2-methyl-substituted; *3*—3-methyl-substituted; *4*—2,2-dimethyl-substituted; *5*—2,3-dimethyl-substituted

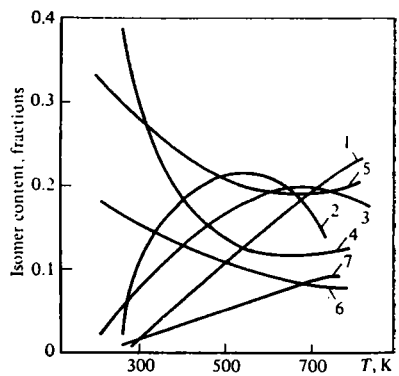


Fig. 18. Composition of equilibrium mixtures of seven alkane isomers (for C_7 and higher alkanes):
1-5—see Fig. 17; *6*—2,4-dimethyl-substituted; *7*—2-ethyl-substituted

equilibrium constants for this temperature, using the equation of an isobar:

$$K_{ij,T} = K_{ij,T_1} \exp\left[\left(-\frac{\Delta H_T}{R}\right)\left(\frac{1}{T} - \frac{1}{T_1}\right)\right] \qquad (6.14)$$

For ΔH_T in Eq. (6.14), it is convenient to take the value from Table 29 for the temperature that is the closest to T.

An analysis of the data in Tables 30-35 shows that elevation of the temperature is always attended by a decrease in the fraction of isoalkanes and a growth in the fraction of *n*-alkanes in the equilibrium mixture, i.e. low temperatures are thermodynamically favourable for producing isomers. The fraction of *n*-alkanes, however, depends on the number of formed isomers. Thus, if only 2-methylpentane forms from *n*-hexane, the fraction of the *n*-alkane at 500 K is 42%, while if all possible isomers form, it is only 24%. It is also clear that the amounts of isomers formed from *n*-butane to *n*-hexane depend on the nature of the feed stock. For example, in the formation of only the 2-methyl-substituted isomer, its fraction in the equilibrium mixture at 300 K is 82% for butanes, 93% for pentanes, 87% for hexanes, and 84% for C_7 and higher alkanes. Consequently, according to a thermodynamic estimate, *n*-pentane is the most favourable feed stock for isomerization.

The effect of the temperature tells especially strongly on the yield of dialkyl-substituted alkanes. Thus, for pentanes, elevation of the temperature from 300 to 700 K reduces the yield almost nine-fold, and hexanes—three-fold.

It should also be noted that with elevation of the temperature, the fraction of the 2-methyl-substituted derivative in monoalkyl-substituted isomers decreases, and that of the 3-methyl-substituted one increases. For alkanes with seven or more carbon atoms, for example, in a mixture of the two indicated isomers, the fraction of the 2-methyl-substituted isomer decreases from 63 to 38% when the temperature is elevated from 300 to 700 K (see Tables 32 and 33). Thus, if isomers are needed in which the alkyl substituent is removed from the chain end, isomerization should be conducted at high temperatures.

It is also interesting (see Table 32) that the formation of dimethyl derivatives is thermodynamically more favourable in comparison with ethyl derivatives, especially at low temperatures. Trimethyl-substituted isomers can form in small amounts.

Special attention is deserved by the equilibrium compositions of mixtures containing no normal alkanes. Such mixtures often form if an alkane that is not a normal one is subjected to isomerization. In the equilibrium compositions of mixtures of isoalkanes, dimethyl-substituted (especially 2,2- and 2,3-) isomers will predominate at low temperatures, while at high temperatures the amounts

of mono- and dimethyl-substituted isomers will be close. If a mixture contains only monomethyl-substituted isomers, their amounts can easily be calculated from their thermodynamic quantities.

For purposes of illustration, we have given Tables 34 and 35, which characterize an equilibrium mixture of various isomers (the calculations were performed using the data of Stull *et al* [26] for dodecanes).

An analysis of the data in Table 33 reveals that at low temperatures equilibrium is shifted somewhat in the direction of the formation of a 2-methylalkane; the amounts of the other methylalkanes are somewhat lower and close. With elevation of the temperature, the probability of the formation of different (including 2-) methylalkanes becomes the same. Thus, if for 300 K the equilibrium constant K_p of the isomerization of an *n*-alkane to a 2-methylalkane ranges from 4.2 to 5.4, and to other methylalkanes from 2.8 to 3.3, then for 500 K the constant K_p in the production of any methylalkane is close to 1.6, and for 700 K to 1.2.

One exception must be noted, however. If in the isomerization of an alkane with an even number of carbon atoms an isomer forms with a methyl group bound to the middle carbon atom of the straight chain, the amount of this isomer will be relatively small. Thus, the constants K_p are low when producing 3-methylheptane from *n*-octane, and 5-methylnonane from *n*-decane. The same exception explains the lower yield of isobutane than isopentane. It can be seen from the data of Table 33 that the equilibrium constant K_p for the formation of 4-methylheptane is about one-fourth of that for 4-methyloctane.

It is interesting to note that this purely theoretical conclusion is supported quite well by experimental data. For example, as indicated by Petrov [32], at 700 K, *n*-tetradecane yields 15% of 6-methyltridecane, but only 8% of 7-methyltridecane. At the same temperature, *n*-hexadecane forms 14-20% each of all the methylalkanes except for 8-methylpentadecane whose yield is 8%. The experimental results cannot be explained by purely kinetic difficulties because, for example, 7-methylalkane forms in appreciable amounts (13%) from *n*-pentadecanes and in relatively small (8%) amounts from *n*-tetradecane. Having in view the failure of the values of K_p to depend on the molecular mass of the feed stock at temperatures above 500 K and the feature noted above when a methylalkane with an axis of symmetry is obtained, we can use the data of Table 33 to approximately calculate the equilibrium compositions of methylalkanes with any number of carbon atoms.

Our calculated data are compared with Petrov's experimental ones [32] in Table 34. The theoretical and experimental values can be seen to coincide satisfactorily. It should be noted that a similar "anomaly" in the thermodynamic properties is also exhibited by

other isoalkanes having an axis or plane of symmetry. One must therefore be careful when generalizing the thermodynamic calculations for mixtures containing such isoalkanes.

The simplest explanation of the thermodynamic features of axisymmetric isomers is that the symmetry number of rotation in them is higher and, consequently, the entropy is lower (in comparison with asymmetric methylalkanes). In axisymmetric isomers, the heat of formation is also somewhat lower.

Since in recent years, isomerization in the liquid phase is being investigated at relatively low temperatures, Table 36 compares the composition of liquid and vapour equilibrium phases in the isomerization of hexanes. The table also presents the values of the equilibrium constants and the saturated vapour pressures of the components used in the calculations. A glance at the data in Table 36 reveals that isomerization in the liquid phase enables one to obtain somewhat larger amounts of a hem-substituted isomer as a result of a decrease in the content of the other isomers, the greatest differences in the compositions of the phases (up to 5% with respect to the content of 2,2-dimethylbutane) being observed at low temperatures. In general, one must have in mind that in the isomerization of alkanes, the equilibrium compositions of the liquid and vapour phases are close at temperatures above 50 °C.

For practical purposes, thermodynamic data are generally employed when estimating the efficiency of processes being realized or kinetic parameters. At the same time, when thermodynamic equilibrium seems to be disturbed, for example, because of a high concentration of isoalkanes, thermodynamic analysis allows us to presume the possible kinetic steps. For illustration, we shall give an analysis of the possible steps of the formation of large amounts of isoalkanes in the hydrocracking of *n*-alkanes [30].

Below are given data on the amounts of normal and isoalkanes in the feed stock and products of hydrocracking.

Data on the isomerization of *n*-heptane in a hydrocracking process at temperatures of 370-420 °C:

Degree of feed stock conversion, %	4.0	49.5
Content in C_7 fraction, %:		
n-heptane	39.2	11.1
isoheptane	59.4	88.9

Data on the isomerization of hexadecane in a hydrocracking process at temperatures of 370-440 °C:

Degree of feed stock conversion, %	53.1	81.6	98.0	100.0
Content of isoalkanes in fraction, %:				
C_4	59.0	58.0	54.0	56.0
C_5	70.0	67.0	65.0	68.0
C_6	62.0	64.0	67.0	65.0

Table 36. **Equilibrium Constants $K_{p,1j}$ of Gas-Phase Isomerization, Saturated Vapour Pressures p_j° (in MPa $\times 10^{-1}$), and Compositions of Equilibrium Mixtures of C_6 Alkanes in the Gas (x_j, %) and Liquid ($x_{j,\mathrm{lq}}$, %) Phases***

Isomer	$K_{p,1j}$	p_j°	x_j	$x_{j,\mathrm{lq}}$	$K_{p,1j}$	p_j°	x_j	$x_{j,\mathrm{lq}}$
	Temperature = 25 °C				Temperature = 50 °C			
n-Hexane	1	0.2	3.5	2	1	0.53	2.5	1.6
2-Methylpentane	6.7	0.28	23.5	21	8.4	0.71	19	17.5
3-Methylpentane	2.1	0.25	7	6	2.4	0.64	5.5	4.5
2,2-Dimethylbutane	4.6	0.42	16	21	5.4	1.0	14.5	18.4
2,3-Dimethylbutane	14.5	0.31	50	50	25.6	0.77	58.5	58
Total			100.0	100.0			100.0	100.0
	Temperature = 75 °C				Temperature = 100 °C			
n-Hexane	1	1.2	1.5	1	1	2.43	1	0.8
2-Methylpentane	10.1	1.56	16	15	11.9	3.03	13.7	12.8
3-Methylpentane	2.7	1.43	4	3.6	3.0	2.79	3.3	3
2,2-Dimethylbutane	8.5	2.1	13	16.4	10.8	2.90	12	14.5
2,3-Dimethylbutane	42	1.66	65.5	64	70	3.0	70	68.9
Total			100.0	100.0			100.0	100.0

* x_j and $x_{j,\mathrm{lq}}$ have been calculated by Eqs. (6.8) and (6.9).

It can be seen from the above data that the feed stock experiences strong isomerization, the fraction of isomers of the same molecular mass increasing when the extent of the process grows.

It is also clear that the decomposition products are highly isomerized. Thus, in the low-boiling hydrocarbons formed in the hydrocracking of normal hexadecane, the fraction of the isomers is usually above 0.55 and changes only slightly with a change in the degree of conversion of the feed stock.

A comparison of the experimental and calculated data shows that the experimentally found content of the isomer forms in individual fractions can exceed the thermodynamically equilibrium one when the isomer is formed from a normal alkane of the same molecular mass. In this connection, it seems necessary to determine the thermodynamically possible paths of formation of large amounts of isomers. It is natural to assume here that considerable amounts of isomers can also form from hydrocarbons with a larger molecular mass, but this assumption must be substantiated thermodynamically. Since the decomposition of an alkane is attended by the formation of an alkane and an alkene with a lower molecular mass, we have calculated the equilibrium yields of isoalkenes in the isomerization of normal alkenes. Two examples are given below:

Reaction	n-C_5H_{10} → *iso*-C_5H_{10} (2-methyl-2-butene)	n-C_6H_{12} → *iso*-C_6H_{12} (2-methyl-2-pentene)
Equilibrium yield, fractions:		
at 600 K	0.97	0.97
at 700 K	0 94	0.94
at 800 K	0.89	0.91

These data show that the isomerization of alkenes involves over 90% of the feed stock, the equilibrium yield of the isomers growing with lowering of the temperature.

Since, however, the hydrocracking products contain not isoalkenes but isoalkanes, the thermodynamic probability of the conversion of isoalkenes into isoalkanes because of hydrogenation of the former has to be estimated. The results of these calculations are given below for the equilibrium yields of isohexane in the hydrogenation of isoalkenes:

Molar ratio hydrogen: feed stock	5	7
Equilibrium yield, fractions:		
at 600 K	0.99	0.99
at 700 K	0.99	0.99

The above calculations indicate that if normal or isoalkenes appeared in a fraction, the possibility of their conversion to isoalkanes exceeds 90%. It is natural to presume that alkenes form from

alkanes of a higher molecular mass in the cracking of the latter. Here intermediate isomerization of the initial normal alkane with n carbon atoms is possible:

$$n\text{-Alkane}_n \rightleftarrows \text{Isoalkane}_n \rightarrow \text{Isoalkane}_{n-m} + \text{Alkene}_m$$

6.1.3. Cycloalkanes

The following isomerization reactions are possible for cycloalkanes (naphthenes): (1) transition (along the ring) of an alkyl group, (2) a change in the number of alkyl groups bound to the ring (with retaining of the ring structure), (3) narrowing or broadening of the ring, and (4) *cis-trans*-isomerization. Reactions (1) and (2) are also possible for alkanes, whereas reactions (3) and (4) are specific for cycloalkanes. The conversions of cyclopentane and cyclohexane hydrocarbons are of the greatest technical interest because these compounds are present in large amounts in the light petroleum fractions and in coal tars. Below we shall consider the isomer conversions of only five- and six-membered cycloalkanes. The isomer conversions of other cycloalkanes (for example, cyclopropanes, cycloheptanes, bicyclic compounds, etc.) are not treated in this book because they are mainly of a purely scientific interest. Some experimentally found equilibrium compositions of such cycloalkanes are given in [33].

Standard thermodynamic tables [4, 26, 35] present data on the thermodynamic characteristics of all cyclopentanes with five, six, and seven carbon atoms and of all cyclohexanes with six, seven, and eight carbon atoms. At the same time, there are nine isomer cyclopentanes with eight carbon atoms, while the isomers with nine carbon atoms include 54 cyclopentanes and 21 cyclohexanes, and no standard tables have been compiled for them. Consequently, if the thermodynamic characteristics of a cycloalkane with over eight carbon atoms have to be determined, we can recommend approximate methods such as Benson's method of corrections (see Appendix 1). One must have in mind here that if an approximate method is used to find the properties of a cycloalkane, the same method has to be used to determine the properties of all the other isomers forming the equilibrium mixture. This is associated with the circumstance that the approximate methods employ "displaced" thermodynamic quantities, the "displacement" error being eliminated when it is the same for all the isomers.

It is also clear that the calculations of the content of all possible isomer cycloalkanes with nine or more carbon atoms in the equilibrium mixture loses all meaning for the same reasons as for alkanes. On the other hand, even for the constantly studied and comparatively simple mixtures of cycloalkanes with seven and eight carbon atoms, data are generally not available on the complete equilibrium

compositions, and often incorrect combinations of *cis*- and *trans*-isomers into a single component are employed.

For this reason, below we shall consider the equilibrium of isomer conversions only for cycloalkanes with six to eight carbon atoms on the basis of standard thermodynamic tables, and later we shall also give some generalizations and experimental data for more high-molecular mononuclear cycloalkanes.

Table 37 presents the heats, entropy changes, and the equilibrium constants for cycloalkane isomerization reactions.

It can be seen that ΔH° and ΔS° for the isomerization of cycloalkanes are not large and change only slightly with the temperature.

For identical transitions of the substituents both in the cyclohexane and in the cyclopentane ring, ΔH°, ΔS°, and K_p are close in the majority of cases. For example, in the preparation at 500 K of *cis*-1,2-dimethylcyclopentane from 1,1-dimethylcyclopentane or of *cis*-1,2-dimethylcyclohexane from 1,1-dimethylcyclohexane, the heat of the reaction is 8.7-9.1 kJ/mol, ΔS° is 7.2-10.3 kJ/(mol·K), and K_p is 0.3-0.4. The observed individual deviations in these quantities for changes of one type in alkylcyclopentanes and alkylcyclohexanes (for example, *trans*-1,2 $\rightarrow$ *trans*-1,3 migration of the substituent) are associated with the insufficiently accurate determination of the thermodynamic parameters of the isomers. In this connection, account must be taken of the approximate nature of the calculated equilibrium compositions given below.

That the migration of the substituents can proceed with either a slight absorption or a slight evolution of heat depending on their initial orientation deserves attention. It is also interesting that when two substituents are retained, the transition from the *cis*-1,2 arrangement to the *cis*-1,3 one or from *trans*-1,2 to *trans*-1,3 proceeds with changes in the entropy close to zero.

The isomerization of alkylcyclopentanes and alkylcyclohexanes with a reduction in the number of substituents proceeds with a small absorption of heat and moderate equilibrium constants, the latter being virtually the same for these two groups of hydrocarbons. The isomerization conversions of only the alkyl substituent are characterized qualitatively by the same laws as those considered earlier for alkanes.

Of especially great technical significance are isomerization conversions with narrowing and broadening of a ring. It can be seen from Table 37 that narrowing of a ring proceeds with the absorption of heat and a substantial increase in the entropy, which produces a noticeable change in the equilibrium constant with the temperature. High temperatures are thermodynamically favourable for the conversion from cyclohexanes to cyclopentanes, and this forms a significant distinction between the isomerization of alkanes and cycloalkanes. If from a structural viewpoint the transition from a normal

Table 37. **Heats $\Delta H°$ [in kJ/mol], Entropy Changes $\Delta S°$ [in J/(mol·K)], for Cycloalkane Isomerization Reactions in the Gas Phase**

Reaction	Thermodynamic quantities at temperatures, K								
	300			500			700		
	$\Delta H°$	$\Delta S°$	K_p	$\Delta H°$	$\Delta S°$	K_p	$\Delta H°$	$\Delta S°$	K_p
1,1-Dimethylcyclopentane (I) → *cis*-1,2-Dimethylcyclopentane (II)	8.7	7.1	0.07	8.7	7.2	0.3	8.7	7.2	0.5
I → *trans*-1,2-Dimethylcyclopentane (III)	1.6	7.5	1.2	1.7	7.9	1.7	1.6	7.7	1.9
I → *cis*-1,3-Dimethylcyclopentane (IV)	2.4	7.5	0.75	2.5	7.9	1.4	2.5	7.7	1.7
I → *trans*-1,3-Dimethylcyclopentane (V)	4.7	7.5	0.4	4.9	7.9	0.8	4.7	7.7	1.1
II → IV	−6.3	0.4	14	−6.2	0.7	5	−6.2	0.5	3.2
III → V	3.1	0	0.3	3.1	0	0.5	3.1	0	0.6
I → Ethylcyclopentane (VI)	11.1	19	0.1	11.0	18.7	0.7	10.2	17.2	1.4
1,1-Dimethylcyclohexane (VII) → *cis*-1,2-Dimethylcyclohexane (VIII)	8.6	9.5	0.09	9.1	10.3	0.4	9.1	10.2	0.7
VII → *trans*-1,2-Dimethylcyclohexane (IX)	1.3	6.0	1.3	1.9	8.3	1.7	2.4	9.0	2.0
VII → *cis*-1,3-Dimethylcyclohexane (X)	−3.7	5.5	8.7	−3.3	6.5	4.9	−3.2	6.7	4.0
VII → *trans*-1,3-Dimethylcyclohexane (XI)	4.4	11.2	0.6	4.8	12.1	1.4	4.5	0.7	1.9
VII → *cis*-1,4-Dimethylcyclohexane (XII)	4.3	5.5	0.3	4.7	0.3	6.7	4.5	6.0	1.0
VII → *trans*-1,4-Dimethylcyclohexane (XIII)	−3.6	−0.2	4.1	−2.9	1.6	2.3	−2.5	2.3	2.0
VII → Ethylcyclohexane (XIV)	9.2	17.5	0.2	9.9	19.4	0.9	10.0	19.5	0.2
VIII → X	−12.5	−4.0	98	−12.4	−3.7	13	−12.2	−3.5	5.5
VIII → XII	−4.5	−4.0	3.7	−4.4	−4.0	1.8	−4.6	−4.2	1.3
IX → XI	−4.5	−4.0	3.7	−4.4	−4.0	1.8	−4.6	−4.2	1.3
IX → XIII	−4.6	−6.0	3.0	−4.8	−6.7	1.4	−4.9	−6.7	1.0
Cyclohexane → Methylcyclopentane	16.4	41.5	0.2	16.6	42.2	3.0	15.4	40.0	9.1
Methylcyclohexane → Ethylcyclopentane	27.1	34.8	0.001	26.8	33	0.08	24.5	29.2	0.5
Methylcyclohexane → I	16.4	15.8	0.009	15.8	14.2	0.12	14.3	12.0	0.3
Methylcyclohexane → II	22.7	23.5	0.6×10^{-3}	21.4	18.2	0.03	19.0	18.5	0.2
Methylcyclohexane → III	18.4	23.3	0.01	17.5	22.1	0.2	16.0	19.7	0.7
II → III	−7.1	0.7	19.5	−7.1	0.7	6.2	−7.1	0.7	3.8
IV → V	2.2	—	0.4	2.2	—	0.6	2.2	—	0.7
VIII → IX	−7.5	−3.6	15	−7.2	−2.0	4.5	−6.7	−1.2	2.8
X → XI	8.2	5.7	0.07	8.2	5.5	0.3	7.7	5.0	0.5

alkane to an isoalkane is similar to the transition from a six-membered to a five-membered cycloalkane (in both cases a tertiary carbon atom appears in the carbon chain instead of a secondary one), then the thermodynamic characteristics of these processes are different. As noted above, the isomerization of alkanes proceeds with the evolution of heat and a decrease in the entropy. With elevation of the temperature, the constant K_p of this reaction diminishes. The structurally close isomerization of cyclohexanes to cyclopentanes proceeds, conversely, with the absorption of heat, an increase in the entropy, and a growth in K_p with the temperature. Moreover, the higher the molecular mass of the feed stock, the lower is K_p for the reaction of conversion of an alkylcyclohexane to an alkylcyclopentane.

As regards the *cis-trans* isomerization of cycloalkanes, it differs appreciably, also in the thermodynamic parameters, from the *cis-trans* isomerization of alkenes described in [36]. Here, however, the difference can be readily explained because for cycloalkanes this kind of isomerization is connected with the breaking and formation of a sigma bond and for alkenes, of a pi bond. Inspection of Table 37 shows that the equilibrium constants of changes of one type (for example, *cis*-1,2 → *trans*-1,2) are close in value for cyclopentane and cyclohexane structures. Here we have to do with a quite general property of isomerization reactions of five- and six-membered cycloalkanes, namely, the thermodynamic parameters of reactions involving a change in the position or number of alkyl substituents are close for the same change and depend only slightly on the number of carbon atoms in the ring.

At the same time, if the reaction *cis*-1,2 → *trans*-1,2 is characterized by the evolution of heat and a high equilibrium constant, then the similar reaction of 1,3-dialkyl-substituted compounds is featured by the absorption of heat and a low equilibrium constant. Accordingly, equilibrium mixtures of 1,2-dialkyl-substituted compounds will contain more of the *trans*-isomer, and those of 1,3-dialkyl-substituted compounds will contain more of the *cis*-isomer. The different thermodynamic stability of the *trans*- and *cis*-isomers depending on the distance between the alkyl substituents is explained from the viewpoints of conformational analysis by the high stability of only such structures in which the repelling interaction of the unbound atoms is minimal. Such interaction will obviously be very considerable for *cis*-1,2-, but not for *cis*-1,3-structures. Calculations show 1,2-dimethylcyclopentanes to contain only 5% of the *cis*-isomer, whereas 1,3-dimethyl-substituted compounds contain already 62%. It should be noted immediately that from the viewpoints of conformational analysis, it is difficult to explain the higher thermodynamic stability of *cis*-1,3 isomers in comparison with *trans*-1,3 ones. In experimental studies, the ratio of these isomers was found to be close to unity [33,

Table 38. **Content of C_6 and C_7 Cycloalkanes in Equilibrium Mixture**

Isomer	Content (fractions) at temperatures, K								
	300			500			700		
	a	b	c	a	b	c	a	b	c
Cyclohexane	0.83	—	—	0.25	—	—	0.10	—	—
Methylcyclopentane	0.17	—	—	0.75	—	—	0.90	—	—
1,1-Dimethylcyclopentane	0.009	0.28	—	0.07	0.17	—	0.10	0.13	—
cis-1,2-Dimethylcyclopentane	0.0006	0.02	0.05	0.02	0.05	0.15	0.05	0.07	0.22
trans-1,2-Dimethylcyclopentane	0.01	0.35	0.95	0.12	0.29	0.85	0.18	0.25	0.78
cis-1,3-Dimethylcyclopentane	0.006	0.20	0.62	0.10	0.24	0.65	0.16	0.22	0.59
trans-1,3-Dimethylcyclopentane	0.004	0.12	0.38	0.06	0.13	0.35	0.10	0.15	0.41
Ethylcyclopentane	0.001	0.03	—	0.05	0.12	—	0.13	0.18	—
Methylcyclohexane	0.97	—	—	0.58	—	—	0.28	—	—

a — In the formation of all the isomers; *b* — in the formation of only five-membered cycloalkanes; c — with equilibrium between the space isomers.

34]. Consequently, we are not certain that the thermodynamic parameters of 1,3-dimethylpentanes have been determined accurately.

The equilibrium compositions of cycloalkanes in isomerization in the gas phase calculated by Eqs. (6.4)-(6.8) are given in Tables 38 and 39.

Table 39. **Content of C_8 Alkylcyclohexanes in Equilibrium Mixture**

Isomer of C_8 alkylcyclohexane	Content (fractions) at temperatures, K					
	300		500		700	
	a	b	a	b	a	b
1,1-Dimethyl	0.064	—	0.08	—	0.07	—
cis-1,2-Dimethyl	0.006	0.07	0.03	0.19	0.04	0.19
trans-1,2-Dimethyl	0.08	0.93	0.13	0.81	0.14	0.81
cis-1,3-Dimethyl	0.53	0.93	0.36	0.77	0.28	0.68
trans-1,3-Dimethyl	0.04	0.07	0.11	0.23	0.13	0.32
cis-1,4-Dimethyl	0.02	0.07	0.05	0.23	0.07	0.33
trans-1,4-Dimethyl	0.25	0.93	0.17	0.77	0.14	0.67
Ethylcyclohexane	0.01	—	0.07	—	0.13	—

a — In the formation of all the isomers; *b* — ratio of *cis*- and *trans*-isomers.

The data of these tables confirm what has been said above about the equilibrium compositions. A comparison of the calculated and experimental (according to [33, 34]) equilibrium compositions shows a quite satisfactory coincidence. For example, both the calculations and experimental data for C_7 cycloalkanes at 500 K show that the equilibrium mixture contains 58% of methylcyclohexane, 7% of 1,1-dimethylcyclopentane, 4 and 5% of ethylcyclopentane, respectively, and so on. The compositions of C_6 and C_8 cycloalkanes also coincide quite satisfactorily (the experimental data are given in [33, 34]).

If, however, for five-membered cycloalkanes the experimental and calculated data coincide in the overall content of 1,2-dimethyl-substituted compounds, but not in the fraction of each isomer, as indicated above, then for alkylcyclohexanes the experimental data [34] are close to the calculated ones (see Table 39) in the content of all the isomers.

Tables 38 and 39 characterize both complete and some partial equilibria. The latter are convenient for analysing experimental results when only a part of the possible isomers forms. The conversions of only five-membered cycloalkanes (no ring broadening reaction proceeds) and *cis-trans*-transitions are such particular cases in the

isomerization of C_7 cycloalkanes, while the mutual conversions of only dimethyl-substituted compounds are such cases for alkylcyclohexanes.

For other partial equilibria, one may use the above quantities, having in view that the ratio of the formed isomers can be the same as in Tables 38 and 39.

Since in experimental studies, the isomerization of cycloalkanes in the liquid phase is often studied, Table 40 compares the equilibrium compositions of the liquid and gas phases in the isomerization of C_7 alkylcyclopentanes. The table also gives the values of $K_{p,1j}$ and p_j^3 used in calculations.

Isomerization in the liquid phase can be seen to yield a somewhat larger (by about 4%) amount of a hem-substituted compound as a result of the reduction in the content of the other isomers. The same effect has also been noted above for the isomerization of alkanes. At the same time, it is obvious that with such close compositions of the gas and liquid phases it is difficult to give preference to the choice of the phase for conducting isomerization from thermodynamic considerations.

On an earlier page, a similar comparison of the compositions of the liquid and gaseous phases was performed for the isomerization of cyclohexane and methylcyclopentane. In this case too, the conducting of a liquid-phase process enables one to obtain only 4-5% more cyclohexane (in comparison with a gas-phase one). The difference in the compositions of these phases for narrowing and broadening of the ring will also be similar in hydrocarbons with a larger molecular mass. A number of experimental data have been obtained [33, 34] for liquid-phase isomerization that are consistent with the above calculations.

As regards the isomerization of cycloalkanes with a more complicated structure or with a larger number of carbon atoms, the equilibrium compositions have been determined for them only experimentally and for partial equilibria. The most detailed investigations in this field were performed by Petrov and his collaborators [33]. The equilibrium compositions of alkylcyclopentanes and alkylcyclohexanes found in these investigations are characterized below. Figure 19 shows the distribution of C_8 alkylcyclopentanes at temperatures up to 600 K. Elevation of the temperature can be seen to be attended by an increase in the content of di-substituted compounds and a reduction in the content of tri- and hem-substituted ones. Only with further elevation of the temperature does the amount of monoalkyl derivatives become noticeable.

Figure 20 summarizes the results of investigations [33] of the equilibrium between cyclopentane and cyclohexane structures. It depicts a reduction in the content of cyclopentanes as the molecular mass grows. According to Petrov [33], for hydrocarbons with 10 or more

Table 4. **Equilibrium Constants $K_{p,1j}$ of Gas-Phase Isomerization, Saturated Vapour Pressure p_j° (in MPa $\times 10^{-1}$), and Compositions of Equilibrium Mixtures of C_7 Alkylcyclopentanes in the Gas (x_j, %) and Liquid ($x_{j,lq}$, %) Phases**

Isomer of alkylcyclopentane	$K_{p,1j}$	p_j°	x_j, %	$x_{j,lq}$, %	$K_{p,1j}$	p_j°	x_j, %	$x_{j,lq}$, %
	Temperature = 25 °C				Temperature = 50 °C			
1,1-Dimethyl	1	0.1	28	32	1	0.28	26	30
cis-1,2-Dimethyl	0.07	0.06	2	2	0.09	0.19	2	2
trans-1,2-Dimethyl	1.2	0.08	35	33	1.25	0.24	34	32
cis-1,3-Dimethyl	0.75	0.08	21	20	0.8	0.25	22	21
trans-1,3-Dimethyl	0.4	0.09	11	11	0.45	0.26	12	12
Ethylcyclopentane	0.1	0.06	3	2	0.15	0.18	4	3
Total			100	100			100	100
	Temperature = 75 °C				Temperature = 100 °C			
1,1-Dimethyl	1	0.68	24	28	1	1.41	23	26
cis-1,2-Dimethyl	0.12	0.47	3	2	0.15	1.01	4	3
trans-1,2-Dimethyl	1.3	0.60	33	32	1.4	1.26	32	32
cis-1,3-Dimethyl	0.9	0.60	22	21	0.9	1.26	21	21
trans-1,3-Dimethyl	0.5	0.61	13	13	0.6	1.30	14	14
Ethylcyclopentane	0.2	0.41	5	4	0.25	0.91	6	4
Total			100	100			100	100

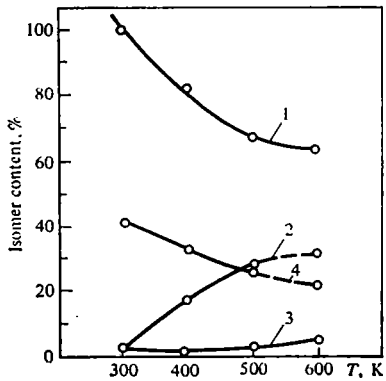


Fig. 19. Composition of equilibrium gas mixture of C_8 alkylcyclopentanes:
1—trimethyl-substituted; *2*—dimethyl-substituted; *3*—monomethyl-substituted; *4*—hem-substituted

carbon atoms at 600 K, the equilibrium content of cyclopentanes should be 10-15%. It should be noted that the above data characterize only one of the many possible equilibria and can change quite substantially with a change in the number of isomers formed. The determination of the equilibrium compositions is reliable only for hydrocarbons with six to eight carbon atoms (see Table 38 and Fig. 19).

To analyse the possible amounts of various isomers with a known composition of a mixture when the number of components is significant, one should use the method of pseudocomponents considered on an earlier page. For example, if C_9 cycloalkanes are being isomerized and it is necessary to determine the possible amount of cyclopentane and cyclohexane structures, one can consider equilibrium between an individual trimethylcyclopentane and an individual dimethylcyclohexane, i.e. between the most probable representatives of the structures being considered (this is illustrated by Fig. 21). Having determined the thermodynamic properties of these hydrocarbons in some way or other, we shall find that, for example, at 600 K the equilibrium constant between them is about 10 and the cyclohexane content is close to 90%. In this example, the results of thermo-

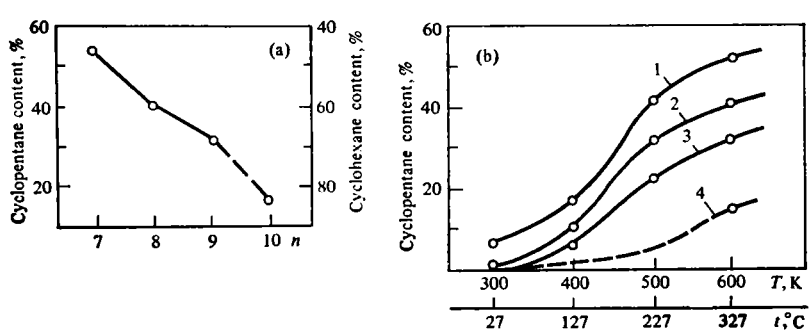


Fig. 20. Ratio of cyclopentanes and cyclohexanes:
a—at 600 K for C_7 and higher hydrocarbons in an equilibrium gas mixture; *b*—at various temperatures; *1*—C_7H_{14}; *2*—C_8H_{16}; *3*—C_9H_{18}; *4*—$C_{10}H_{20}$; *n* = number of carbon atoms in a molecule

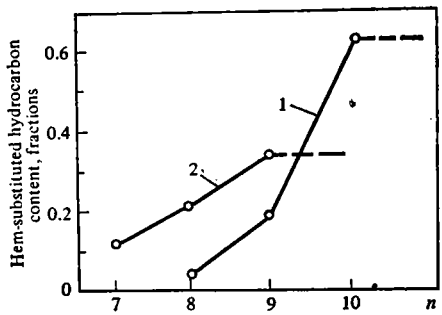


Fig. 21. Content of hem-substituted hydrocarbons in equilibrium mixtures at 600 K:
1—for cyclohexanes; *2*—for cyclopentanes; *n*=number of carbon atoms in a molecule

dynamic calculations by the method of pseudocomponents confirms the possibility of generalizing Petrov's experimental results, but only for two components.

6.1.4. Aromatics

Reliable thermodynamic parameters have been obtained for alkylbenzenes [26]. Below we shall consider in detail the thermodynamics of the isomerization of their mixtures because it is not only of a scientific, but also of a practical interest. As regards the isomerization of alkylnaphthalenes and polycyclic aromatics, in these cases approximate methods have to be used for thermodynamic calculations, and experiments are often resorted to for determining the equilibrium composition. It should also be noted that the studying of the isomerization of polycyclic aromatics is meanwhile only of a scientific significance.

Possible kinds of isomerization for alkylbenzenes are the migration of an alkyl group along the ring, and a change in the number of alkyl substituents of their structure. The thermodynamic characteristics of alkylbenzene isomerization reactions have been determined by a number of authors [4, 34]. The values of $\Delta H°$, $\Delta S°$, and K_p for gas-phase processes are given in Table 41.

It can be seen that when one of two alkyl substituents migrates along the aromatic ring with an increase in the distance between them, the heat of the reaction is not large and can be either greater than zero (the transition of *m*-xylene into *p*-xylene) or smaller than zero (the transition of *o*-xylene into *m*-xylene). The changes in the entropy are also not great and can also be either positive or negative.

If the number of substituents decreases, the reaction is attended by the absorption of heat; when the number of substituents increases, heat is evolved.

Table 41. **Heats $\Delta H°$ (in kJ/mol), Entropy Changes $\Delta S°$ [in J/(mol·K)], and Equilibrium Constants K_p for Isomerization Reactions of Aromatics in the Gas Phase**

Reaction	T, K	$\Delta H°$	$\Delta S°$	K_p
1,2-Dimethylbenzene (I) → 1,3-Dimethylbenzene	300	—1.8	5.0	3.7
	500	—2.6	3.0	2.6
	700	—3.0	2.1	2.2
(I) → 1,4-Dimethylbenzene	300	—1.1	—0.4	1.5
	500	—2.1	—0.8	1.2
	700	—2.6	—2.9	1
(I) → Ethylbenzene	300	10.8	7.5	0.03
	500	10.5	6.7	0.2
	700	11.0	7.1	0.4
1-Methyl-2-ethylbenzene (II) → 1-Methyl-3-ethylbenzene	300	—3.1	4.6	6.5
	500	—4.0	2.5	3.6
	700	—4.4	2.1	2.8
(II) → 1-Methyl-4-ethylbenzene	300	—4.6	—0.4	5.8
	500	—5.9	—3.3	4.2
	700	—6.3	—4.2	1.7
(II) → *n*-Propylbenzene	300	6.7	1.3	0.08
	500	4.6	—2.9	0.4
	700	5.9	0	0.3
(II) → Isopropylbenzene	300	2.5	—10.9	0.09
	500	2.1	—12.2	0.2
	700	2.5	—11.7	0.2
(II) → 1,2,3-Trimethylbenzene	300	—10.9	—8.2	29
	500	—12.1	—12.5	6.8
	700	—13.8	—14.6	1.7
(II) → 1,2,4-Trimethylbenzene	300	—15.1	—3.1	310
	500	—16.4	—7.1	35.5
	700	—17.8	—9.2	7.0
(II) → 1,3,5-Trimethylbenzene	300	—17.3	—13.8	195
	500	—19.1	—19.2	15.4
	700	—20.6	—21.7	2.5

We shall note immediately that the equilibrium of a reaction resulting in a decrease in the number of substituents is shifted greatly to the left; at low temperatures this reaction cannot result in the conversions of a dialkyl-substituted hydrocarbon to a monoalkyl-substituted one by more than 8-10%. When only migration of the substituents occurs, 1,3- and 1,4-substituted compounds will predominate at low temperatures, and 1,3-substituted ones at high temperatures.

Thermodynamic calculations show the possibility of conducting high-conversion isomerization with an increase in the number of alkyl substituents, for example, the conversion of dialkyl- to trialkyl-substituted compounds, among which 1,2,4-trimethylbenzene can form in the largest amounts (Fig. 22).

As regards the ratio between monoalkyl-substituted compounds with a normal and isostructure of the substituent, it is mainly the same as for normal and isoalkanes, and grows with elevation of the temperature, although $\Delta H°$ is somewhat lower owing to the influence of the aromatic nucleus.

It should be stressed that in real mixtures all possible isomers are encountered rarely, and it is necessary to determine the equilibrium compositions for partial equilibria with a limited number of isomers. For example, in the isomerization of xylenes, the formation of ethylbenzene may be hampered because of purely kinetic restrictions; here equilibrium should be considered only between xylenes.

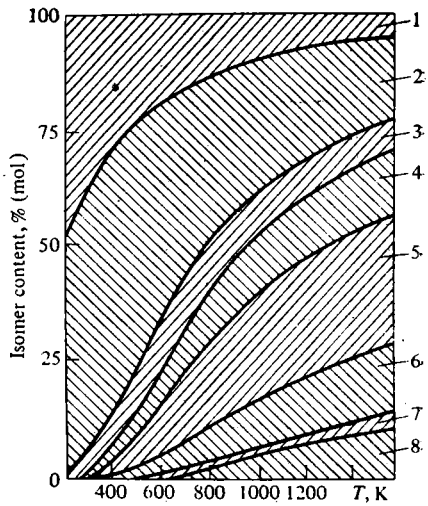


Fig. 22. Composition of an equilibrium mixture of C_9 alkylbenzenes:
1—1,3,5-trimethylbenzene; 2—1,2,4-trimethylbenzene; 3—1,2,3-trimethylbenzene; 4—1-methyl-2-ethylbenzene; 5—1-methyl-3-ethylbenzene; 6—1-methyl-4-ethylbenzene; 7—isopropylbenzene; 8—*n*-propylbenzene

The quantitative compositions of the equilibrium mixtures of aromatics in the gas phase have been determined by Eqs. (6.4)-(6.8) and are given in Tables 42 and 43. They confirm what has been

Table 42. **Equilibrium Compositions of Products of C_8 Alkylbenzene Gas-Phase Isomerization**

Reactions	Temperature, K	Content of isomer in equilibrium mixture, fractions			
		1,2-Dimethylbenzene	1,3-Dimethylbenzene	1,4-Dimethylbenzene	Ethylbenzene
Formation of all isomers	300	0.16	0.595	0.24	0.005
	500	0.20	0.53	0.23	0.04
	700	0.225	0.48	0.215	0.08
Formation of only xylenes	300	0.16	0.60	0.24	—
	500	0.21	0.55	0.24	—
	700	0.245	0.52	0.235	—
Formation of only *o*- and *m*-xylenes	300	0.21	0.79	—	—
	500	0.28	0.72	—	—
	700	0.32	0.68	—	—
Formation of only *m*- and *p*-xylenes	300	—	0.71	0.29	—
	500	—	0.70	0.30	—
	700	—	0.70	0.30	—

Table 43. **Equilibrium Compositions of Products of C_9 Alkylbenzene Gas-Phase Isomerization**

Reactions	Temperature, K	Content of isomer in equilibrium mixture, fractions							
		trimethylbenzenes			methylethylbenzenes			propylbenzenes	
		1,2,3-	1,2,4-	1,3,5-	1-methyl-2-ethyl	1-methyl-3-ethyl	1-methyl-4-ethyl	normal	iso-
Formation of all isomers	300	0.05	0.56	0.36	0.002	0.012	0.011	traces	traces
	500	0.10	0.51	0.22	0.02	0.08	0.06	0.005	0.005
	700	0.10	0.41	0.14	0.06	0.16	0.10	0.02	0.01
Formation of trimethylbenzenes	300	0.05	0.58	0.37	—	—	—	—	—
	500	0.12	0.61	0.27	—	—	—	—	—
	700	0.15	0.63	0.22	—	—	—	—	—
Formation of dialkylbenzenes	300	—	—	—	0.08	0.48	0.44	—	—
	500	—	—	—	0.13	0.49	0.38	—	—
	700	—	—	—	0.19	0.50	0.31	—	—
Formation of normal and isopropylbenzenes	300	—	—	—	—	—	—	0.47	0.53
	500	—	—	—	—	—	—	0.62	0.38
	700	—	—	—	—	—	—	0.69	0.31

Table 44 Equilibrium Constants $K_{p,1j}$ of Gas-Phase Isomerization, Saturated Vapour Pressure p_j° (in kPa), and Compositions of Equilibrium Mixtures of C_8 and C_9 Alkylbenzenes in the Gas (x_j, %) and Liquid ($x_{j,lq}$, %) Phases

Alkylbenzene	$K_{p,1j}$	p_j°	x_j	$x_{j,lq}$	$K_{p,1j}$	p_j°	x_j	$x_{j,lq}$
	Temperature = 25 °C				Temperature = 50 °C			
C_8 Alkylbenzenes								
1,2-Dimethylbenzene	1	1.36	16	14	1	3.43	17	14
1,3-Dimethylbenzene	3.7	1.11	59.5	57	3.5	4.13	58	59
1,4-Dimethylbenzene	1.5	1.15	24	28.95	1.45	4.32	24	26
Ethylbenzene	0.03	1.21	0.5	0.05	0.04	4.73	1.0	1.0
C_9 Alkylbenzenes								
1-Methyl-2-ethylbenzene	1	0.33	0.18	0.2	1	1.46	0.3	0.3
1-Methyl-3-ethylbenzene	6.5	0.40	1.18	1.6	5.9	1.68	1.7	2.3
1-Methyl-4-ethylbenzene	5.8	0.40	1.1	1.95	5.0	1.68	1.5	1.81
n-Propylbenzene	0.08	0.43	0.01	0.02	0.10	1.84	0.03	0.04
Isopropylbenzene	0.09	0.63	0.02	0.03	0.95	2.48	0.03	0.05
1,2,3-Trimethylbenzene (hemellitene)	29	0.21	4.51	3.2	20.6	0.93	6.1	4.5
1,2,4-Trimethylbenzene (pseudocumene)	310	0.28	57	53	193	1.21	57	54
1,3,5-Trimethylbenzene (mesitylene)	195	0.33	36	40	113	1.43	33.34	37
C_8 Alkylbenzenes	Temperature = 75 °C				Temperature = 100 °C			
1,2-Dimethylbenzene	1	10.34	18	15	1	56.53	18	16
1,3-Dimethylbenzene	3.3	13.24	57	60	3.1	31.19	56	59
1,4-Dimethylbenzene	1.40	12.73	24	24	1.35	29.19	24	24
Ethylbenzene	0.06	13.80	1.0	1.0	0.07	34.26	2.0	1.0
C_9 Alkylbenzenes								
1-Methyl-2-ethylbenzene	1	5.19	0.4	0.5	1	13.64	0.6	0.6
1-Methyl-3-ethylbenzene	5.4	5.56	2.8	3.5	5.0	15.41	3	4
1-Methyl-4-ethylbenzene	4.4	5.55	1.9	2.45	4.0	15.20	2.4	3
n-Propylbenzene	0.12	5.96	0.05	0.08	0.14	16.74	0.08	0.1
Isopropylbenzene	0.10	6.52	0.05	0.07	0.11	20.65	0.07	0.1
1,2,3-Trimethylbenzene	15.4	3.89	6.8	4.4	12.0	9.42	7.85	6
1,2,4-Trimethylbenzene	129	4.17	57	55	91	11.90	56	55
1,3,5-Trimethylbenzene	71.5	4.82	31	34	49	13.54	30	31.2

said above on the equilibrium compositions. Everything said above also holds when isomerization is being conducted in the liquid phase.

We have determined quantitatively the composition of a liquid-phase equilibrium mixture assuming that Raoult's law is observed and with the use of Eq. (6.9). The results are given in Table 44.

The approximate methods mentioned above also enable one to determine the equilibrium compositions for hydrocarbons with more than nine carbon atoms. But owing to the low accuracy of these methods, it is not always possible to single out the small differences in the thermodynamic parameters of the individual substances. Moreover, the actually formed mixtures usually contain a small number of isomers. We shall therefore not consider in detail the isomerization of hydrocarbons with 10 or more carbon atoms. If these hydrocarbons contain mono-, di-, and trialkylsubstituted compounds, their ratio will be the same as that of similar isomers according to the data of Table 43. Since, however, the isomerization conversions of tetramethylbenzenes are being studied in recent years [36], Table 45 presents data on their equilibrium compositions.

It can be seen that isodurene remains the thermodynamically most stable both at low and at high temperatures; its equilibrium content changes slightly with the temperature and is 50-53% in

Table 45. **Equilibrium Constants $K_{p,1j}$ of Gas-Phase Isomerization, Saturated Vapour Pressure p_j° (in kPa), and Compositions of Equilibrium Mixtures of Tetramethylbenzenes in the Gas (x_j, %) and Liquid ($x_{j,\mathrm{lq}}$, %) Phases**

Alkylbenzene	Temperature, K	$K_{p,1j}$	p_j°	x_j	$x_{j,\mathrm{lq}}$
1,2,3,4-Tetramethylbenzene (prenitol) (1)	300	1	0.05	8	11.6
	325	1	0.29	9	11.8
	350	1	1.17	9	11.7
	375	1	3.77	10	11.9
	500	1	—	13	—
	700	1	—	17	—
1,2,3,5-Tetramethylbenzene (isodurene) (2)	300	6.56	0.08	53	51.4
	325	5.97	0.39	53	52.8
	350	5.56	1.52	53	52.9
	375	5.20	4.74	53	52.9
	500	3.91	—	52	—
	700	2.96	—	50	—
1,2,4,5-Tetramethylbenzene (durene) (3)	300	4.86	0.08	39	37.0
	325	4.38	0.41	38	35.4
	350	4.01	1.59	38	35.4
	375	3.71	4.93	37	35.2
	500	2.68	—	35	—
	700	1.91	—	33	—

the gas and liquid phases. The temperature has the greatest effect on the equilibrium content of prenitol in the mixture, which grows from 8 to 17% when the temperature is increased from 300 to 700 K. It is clear that the liquid phase is enriched in prenitol in comparison with the gas phase because this compound has the lowest vapour pressure. At the same time, the difference in the compositions of the liquid and vapour phases of tetramethylbenzene mixtures is not great and the greatest difference in the content of a component does not exceed 3%. Table 46 gives the equilibrium compositions of C_{10} and C_{11} methylethylbenzenes.

Table 46. **Equilibrium Distribution of C_{10} and C_{11} Methylethylbenzenes at 315 °C [4]**

Dimethylethylbenzene	Content in equilibrium mixture, %	Methyldiethylbenzene	Content in equilibrium mixture, %
1,2-Dimethyl-3-ethyl	3.2	1-Methyl-2,3-diethyl	0.9
1,2-Dimethyl-4-ethyl	20.9	1-Methyl-2,4-diethyl	20.3
1,3-Dimethyl-2-ethyl	1.9	1-Methyl-2,5-diethyl	21.2
1,3-Dimethyl-4-ethyl	16.4	1-Methyl-2,6-diethyl	1.1
1,3-Dimethyl-5-ethyl	33.7	1-Methyl-3,4-diethyl	9.8
1,4-Dimethyl-2-ethyl	23.9	1-Methyl-3,5-diethyl	46.7

Let us now compare the calculated and experimental values. Equilibrium mixtures of xylenes have been studied experimentally the most thoroughly. Data of various authors on the experimental equilibrium compositions of xylenes in liquid-phase isomerization are reviewed in [34]. In the presence of various acid catalysts ($AlCl_3$-HCl, $AlBr_3$-HBr, BF_3-HF) at 50 °C, xylenes form no ethylbenzene. The products included 12-16% of *ortho*-, 65-72% of *meta*-, and 15-19% of *para*-xylene. At 100-120 °C, their amounts are 18-19, 60-61, and 20-22%, respectively. A comparison of these data with the calculated ones (see Table 46) reveals that in experimental studies, a virtually equilibrium content of *ortho*-xylene was obtained, whereas the content of *meta*-xylene exceeded the equilibrium value slightly. This indicates that at low temperatures the conversions of *ortho*-xylene proceed at a higher rate than of other isomers. The formation of ethylbenzene from xylenes is also observed in the presence of solid catalysts at elevated temperatures. When studying the conversions of C_8 aromatics in the presence of an aluminosilicate catalyst at 515 °C, the authors of [34] were able to reach equilibrium only with respect to *p*-xylene and ethylbenzene, evidently both because of kinetic difficulties and for the reasons considered above. In general, the achievement of an equilibrium content of *p*-xylene is characteristic of high-temperature processes.

In investigations of the isomerization of C_9 and C_{10} alkylbenzenes, mixtures containing all possible isomers in amounts close to the equilibrium ones were not obtained. The experimental studies were limited to partial equilibria, for example, only between polymethylbenzenes. The achievable ratio of the trimethylbenzenes was determined in [34] by conducting experiments in the liquid phase with the BF_3-HF catalyst. It was found that no hemellitene (1,2,3-trimethyl-benzene) forms, while the ratio of pseudocumene and mesitylene was close to the equilibrium one (see Table 44).

In our investigations [30], a mixture of *n*-butyl- (28.3%), 1,2-diethyl- (18.7%), and 1-methyl-2-*n*-propyl- (53.0%) benzenes close to the equilibrium one was obtained. In these investigations, carried out in the presence of a chromo-alumina catalyst, no isomerization with the appearance of methyl substituents was observed. Experimental and theoretical studies of the isomerization of tetramethylbenzenes were performed by Mamedaliev et al [36]. They succeeded in approaching the equilibrium compositions characterized in Tables 45 and 46 on active catalysts. For example, in the isomerization of durene (1,2,4,5-tetramethylbenzene) on a zeolite catalyst at 400 °C and 12.5 kPa, the content of durene in the C_{10} fraction was 54.5%, and of isodurene—38.9%.

The compositions of isomer mixtures of dimethylethylbenzenes and methyldiethylbenzenes have been measured at temperatures of 200-315 °C in the presence of amorphous aluminosilicate and the decationized zeolite Y- and H-mordenite [37]. A composition the closest to the equilibrium one was obtained when using amorphous aluminosilicate, which is explained by the absence in this case of molecular-sieve effects. The experimental fractions of 1,3-dimethyl-4-ethyl- and 1,4-dimethyl-2-ethylbenzenes were somewhat higher than the equilibrium ones (see Table 36), and their sum was 0.65 of all the isomer dimethylethylbenzenes. For methyldiethylbenzenes, the greatest contents of 1-methyl-2,4-diethyl- (31%), 1-methyl-2,5-diethyl- (29%), and 1-methyl-3,5-diethyl-(31%) isomers were obtained.

6.1.5. Alkenes

The isomerization of alkenes (olefins) proceeds with a small heat effect (Table 47). For a large number of reactions of various hydrocarbons, the molar heats depend only slightly on the molecular mass of the initial hydrocarbon. This is also observed, naturally, for the isomerization of alkenes. But this phenomenon is not so noticeable for alkenes because the heats of the various isomerization reactions are low. It is convenient to divide the isomerization reactions of alkenes into three groups, namely, *cis-trans*-isomerization, structural, and skeleton isomerization. In *cis-trans*-isomerization, heat is

Table 47. **Heats of Isomerization of Alkenes**

Reaction	Heat of isomerization (in kJ/mol) at temperatures, K			
	300	500	700	900
cis-2-Alkene → *trans*-2-Alkene	—3.9	—3.0	—2.7	—2.6
cis-3-Alkene → *trans*-3-Alkene	—4.1	—2.9	—2.1	—1.7
1-Alkene → *cis*-2-Alkene	—7.0	—8.1	—9.0	—9.6
1-Alkene → *trans*-2-Alkene	—10.9	—11.1	—11.5	—11.8
cis-2-Alkene → *cis*-3-Alkene	0	0	0	0
trans-2-Alkene → *trans*-3-Alkene	0	0	+0.8	+1.2
1-Alkene → 2-Methyl-1-alkene	—15.2	—14.7	—14.2	—14.1
1-Alkene → 2-Ethyl-1-alkene	—12.4	—11.9	—11.5	—11.0
1-Alkene → 3-Methyl-1-alkene	—6.2	—3.6	—0.3	+2.7
1-Alkene → 2,3-Dimethyl-1-alkene	—20.2	—18.2	—16.5	—16.1
1-Alkene → 3,3-Dimethyl-1-alkene	—18.0	—18.6	—19.4	—20.3

evolved. Structural isomerization, which yields a *cis*-2-alkene or a *trans*-2-alkene from a 1-alkene, proceeds with the evolution of heat, in the latter case the heat of the process being somewhat greater. On the other hand, the migration of the double bond from the 2- to the 3-position without a change in the spacial configuration of the alkene molecule (2-*cis*- → 3-*cis*- or 2-*trans*- → 3-*trans*-) occurs virtually without the evolution or absorption of heat (the heat of the process is less than 0.5 kJ/mol).

Equilibrium Compositions of Butene Mixtures. It is convenient to begin an analysis of the equilibrium compositions of the mixtures formed in the isomerization of alkenes with a treatment of the equilibrium mixtures of butenes.

In the general case, equilibrium is possible between the four isomer butenes: 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene. It should be had in view, however, that for a number of catalytic systems a mixture of only three normal isomers forms, for example, in reactions in the presence of pure aluminium oxide. Catalysts are known that yield mainly *trans*-isomers, i.e. it is also possible to establish equilibrium between two butenes. Consequently, when comparing experimental data with the calculated equilibrium composition, one must consider equilibrium exactly for the mixture formed during the experiment.

For example, calculations of equilibrium for the four butenes show that at 200 °C the equilibrium mixture should contain about 15% of *cis*- and 27% of *trans*-2-butene. Experimental data [4], on the other hand, show that at this temperature the equilibrium mixture contains 32% of the *cis*- and 55% of the *trans*-isomer. Naturally, a comparison of these data can lead to the conclusion that thermodynamic equili-

brium has been disturbed. Actually, however, no isobutene formed in the experiments, and the calculations of equilibrium for the four isomers in this situation cannot be applied. The data in [4] are close to the theoretical ones for the equilibrium of three *n*-butenes. The use of experimental data [4] for the calculation of equilibrium in the formation of isobutene is also not quite correct from these standpoints, because these investigators took no account of structural and *cis-trans*-isomerization and combined the 2-butenes with 1-butene. A similar inaccuracy has also been committed in the works of Zharkova and Moldavsky, and of MacCurthy and Turkevich, who combined *cis*-2-butene and *trans*-2-butene (see [36]).

The equilibrium compositions for various mixtures of butenes are presented in Table 48.

Table 48. **Equilibrium Compositions of Product Mixtures in the Isomerization of Butenes**

Butene	Content in mixture (in mole fractions) at temperatures, K			
	300	500	700	900
1-Butene	0.06	0.21	0.38	0.50
trans-2-Butene	0.94	0.79	0.62	0.50
1-Butene	0.12	0.33	0.50	0.60
cis-2-Butene	0.88	0.67	0.50	0.40
cis-2-Butene	0.23	0.34	0.39	0.40
trans-2-Butene	0.77	0.66	0.61	0.60
1-Butene	0.01	0.12	0.29	0.43
Isobutene	0.99	0.88	0.71	0.57
trans-2-Butene	0.23	0.35	0.40	0.43
Isobutene	0.77	0.65	0.60	0.57
cis-2-Butene	0.08	0.22	0.29	0.34
Isobutene	0.92	0.78	0.71	0.66
1-Butene	0.03	0.14	0.26	0.38
cis-2-Butene	0.22	0.30	0.28	0.25
trans-2-Butene	0.75	0.56	0.46	0.37
1-Butene	0.01	0.07	0.16	0.25
cis-2-Butene	0.06	0.15	0.17	0.17
trans-2-Butene	0.21	0.27	0.27	0.25
Isobutene	0.72	0.51	0.40	0.33

The calculated data of Table 48 agree well with the experimental data in which a state of equilibrium has been reached. For example, the following composition has been obtained for a mixture of *n*-butenes at 903 K [4]: 34.8% of 1-butene, 37.5% of *trans*-2-butene,

and 27.7% of *cis*-2-butene. These data are close to those given in Table 48 (38, 37, and 25%, respectively). We shall indicate that the error in calculations is smaller than that in the experimental determination of the equilibrium composition, which usually exceeds 1.5%.

At the same time, the use of kinetic data can result in a wrong conclusion on the apparent disturbance of thermodynamic equilibrium. For example, the isomerization of 1-butene to 2-butenes under conditions of heterogeneous catalysis results in the formation of a large amount of the *cis*-isomer. Here the yields of the *cis*-isomer can substantially exceed the data given in Table 48 for the mixture of the three normal butenes: according to [4], in the isomerization of 1-butene at 723 K, the yield of the *cis*-isomer reaches 39.4% and of the *trans*-isomer, 31%, while the content of 1-butene drops to 27.4% (the equilibrium yield of the *cis*-isomer is 28% for the triple mixture). Actually, this situation does not at all signify that thermodynamic equilibrium has been disturbed. What does happen is the rapid setting in of 1-butene $\rightleftharpoons$ *cis*-2-butene equilibrium (the yield of the *cis*-isomer is about 50%) with subsequent slow setting in of equilibrium for the mixture of the three normal butenes. Here the equilibrium mixture of three isomers forms from the equilibrium mixture of two isomers. Such a stepwise establishment of equilibrium often occurs in the reactions of alkenes.

Equilibrium Compositions of Pentene Mixtures. In the general case, equilibrium between the six pentene isomers is possible, namely, 1-pentene, *cis*- and *trans*-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene. In real situations, such an equilibrium does not generally set in, hence, as for butenes, it is expedient to consider equilibrium for some particular cases. The results of such calculations are given in Table 49.

The nature of the change in the ratio of the various pentenes with the temperature is mainly the same as for the butenes. At low temperatures, *trans*-2-pentene is the most thermodynamically stable among the normal pentenes, and 2-methyl-2-butene among the isopentenes. With elevation of the temperatures, the content of 1-pentene and 2-methyl-1-butene in the equilibrium mixture grows. It is interesting that isomerization cannot lead to the appearance of appreciable amounts of one of the isomers—3-methyl-1-butene. The experimental data on studying the equilibrium of pentenes in the gas phase are consistent satisfactorily with the data given in Table 49.

Equilibrium Compositions of Mixtures of C_6 and Higher Alkenes. The growth in the number of carbon atoms in an alkene molecule is attended by a sharp increase in the number of its possible isomers. For example, whereas butenes can have four isomers, hexenes can have 20, and heptenes 48. Since in real situations, all the possible isomers of hexenes and moreover of heptenes do not form, it is good

to compare the thermodynamic stability of different isomer molecules, namely, with a normal chain, with one and two methyl radicals, and with an ethyl radical.

Table 49. **Equilibrium Compositions of Product Mixtures in the Isomerization of Pentenes**

Pentene	Content in mixture (in mole fractions) at temperatures, K			
	300	500	700	900
1-Pentene	0.02	0.08	0.16	0.24
cis-2-Pentene	0.26	0.29	0.33	0.30
trans-2-Pentene	0.72	0.63	0.51	0.46
2-Methyl-1-butene	0.11	0.26	0.37	0.44
3-Methyl-1-butene	—	0.02	0.05	0.08
2-Methyl-2-butene	0.89	0.72	0.58	0.48
1-Pentene	—	0.01	0.04	0.08
cis-2-Pentene	0.01	0.05	0.08	0.10
trans-2-Pentene	0.02	0.08	0.13	0.16
2-Methyl-1-butene	0.11	0.23	0.28	0.29
3-Methyl-1-butene	—	0.01	0.03	0.05
2-Methyl-2-butene	0.86	0.62	0.44	0.32

Table 50. **Equilibrium Compositions of Gaseous Product Mixtures in the Isomerization of C_6 and Higher Alkenes**

Alkene	Content in mixture (in mole fractions) at temperatures, K			
	300	500	700	900
1-Alkene	0.01	0.07	0.14	0.20
cis-2-Alkene	0.23	0.32	0.32	0.31
trans-2-Alkene	0.76	0.61	0.54	0.49
1-Alkene	0.01	0.05	0.10	0.14
cis-2-Alkene	0.15	0.22	0.23	0.22
trans-2-Alkene	0.51	0.43	0.38	0.36
cis-3-Alkene	0.07	0.09	0.09	0.09
trans-3-Alkene	0.26	0.21	0.20	0.19
1-Alkene	0	0.01	0.02	0.05
2-Methyl-1-alkene	0.05	0.13	0.19	0.23
2-Methyl-2-alkene	0.34	0.30	0.25	0.21
3-Methyl-*cis*-2-alkene	0.12	0.15	0.15	0.15
3-Methyl-*trans*-2-alkene	0.18	0.23	0.24	0.22
2,3-Dimethyl-1-alkene	0.05	0.07	0.08	0.09
2,3-Dimethyl-2-alkene	0.26	0.11	0.07	0.05

When using the data of Table 50, the composition of a mixture of hexenes and heptenes will be the same because the equilibrium constants of reactions of one type (for example, 1-alkene ⇄ *cis*-2-alkene, *cis*-2-alkene ⇄ *trans*-2-alkene, etc.) are identical. In isomerization reactions, there are generally formed mixtures of normal isomers with the double bond in positions 1 and 2, mixtures of normal isomers with the double bond in positions 1, 2, and 3, and skeleton isomers. In this connection, we have calculated the equilibrium compositions for these isomer forms.

Examination of Table 50 reveals that for normal alkenes with six and more carbon atoms, the influence of the temperature on the equilibrium composition of a mixture is mainly the same as for butenes and pentenes: elevation of the temperature is attended by an increase in the content of the 1-alkene and a decrease in the content of the *trans*-2- and *trans*-3-alkenes; the content of the *cis*-2- and *cis*-3-alkenes changes to a smaller degree. If skeleton isomerization occurs, considerable amounts of 2-methyl-2-alkene and 3-methyl-2-alkene form. At low temperatures, the formation of considerable amounts of 2,3-dimethyl-2-alkene is possible.

It is expedient to compare the calculated data given in Table 50 with the experimental ones. The equilibrium composition of isomer hexenes has been studied experimentally in [34]. According to these data, an equilibrium mixture of normal hexene isomers at 800 K contains about 12% of 1-hexene, 22% of *cis*-2-hexene, 38% of *trans*-2-hexene, 9% of *cis*-3-hexene, and 19% of *trans*-3-hexene. These results practically coincide with the data in Table 50. The experi-

Table 51. **Equilibrium Compositions of Liquid Mixtures of Pentenes and Hexenes at 300 K**

Alkene	Content in equilibrium mixture, mole fractions*	Saturated vapour pressure, kPa
1-Pentene	0.01 (0.02)	79
cis-2-Pentene	0.27 (0.26)	61
trans-2-Pentene	0.72 (0.72)	62.5
1-Hexene	0.01 (0.01)	23
cis-2-Hexene	0.16 (0.15)	18.5
trans-2-Hexene	0.52 (0.51)	19
cis-3-Hexene	0.06 (0.07)	20
trans-3-Hexene	0.25 (0.26)	19.5
2-Methyl-1-butene	0.08 (0.10)	75.5
2-Methyl-2-butene	0.92 (0.90)	57.5
2-Methyl-1-pentene	0.54 (0.48)	25
2-Methyl-2-pentene	0.46 (0.52)	30.5

* The data in parentheses are for an equilibrium gaseous mixture.

absorption of heat. In the skeleton isomerization of *cis*-1,3-pentadiene, heat is evolved up to 525 K, and is absorbed at higher temperatures. Near the cited temperatures, these isomerization reactions proceed with a zero heat effect, which is an extremely rare case.

The equilibrium constants of both skeleton and structural isomerization also change only slightly with the temperature (not only the heats, but also the changes in the entropy are small for them), and this results in relative stability of the equilibrium mixture composition within quite a broad temperature interval. The isoprene content in the equilibrium mixture of the three isomers at 300 K is 37%, and at 700 K is 30%. If an equilibrium mixture in isomerization contains only one structural isomer and isoprene (this is a hypothetic case), the content of the latter can be increased to 50-59%. Hence, the isomerization of 1,3-pentadienes to isoprene in a flow reactor will involve not over one-third of the feed stock and will require considerable recirculation. Having in view that the isomerization of the skeleton of dienes is attended by intensive side reactions of hydrogen redistribution, it is more expedient (for technological, and not thermodynamic reasons) to convert 1,3-pentadienes to *n*-pentane or *n*-pentene whose isomerization is performed in the industry. A number of authors, including Mamedaliev *et al.* [36] have proposed catalytic systems for the hydrogenation of 1,3-pentadienes.

Ring-Chain Isomerization (Cyclization) of Lower Alkenes. The dehydrocyclization of alkenes with six or more carbon atoms with the formation of benzene derivatives is a well studied process (see Chap. 7). As regards the cyclization of propylene to cyclopropane, 1-butene to cyclobutane, and 1-pentene to cyclopentane, these reactions are reverted to from time to time by investigators because they are the simplest ones for the synthesis of cycloalkanes in short supply, especially cyclopropane and cyclobutane. The conversion of alkenes to cycloalkanes should be considered as a kind of isomerization known as **ring-chain isomerization** [30]. Its proceeding is postulated for explaining the mechanism of the skeleton isomerization of alkenes and alkanes. Table 54 presents the thermodynamic characteristics of the gas-phase cyclization of C_3-C_5 normal alkenes in the temperature interval (300-700 K) used for experimental investigations.

Examination of the data in Table 54 reveals that the formation of cycloalkanes from C_3 and C_4 alkenes in conventional (they are sometimes called dark) reactions is thermodynamically impossible, and, conversely, the decomposition of cyclopropane and cyclobutane into the relevant alkenes proceeds practically completely. This is explained by the "stressed state" of the three- and four-membered ring.

At the same time, in photochemical reactions, when energy is continuously supplied to the system, and the form of the thermodynamic equations varies, the working relations for dark reactions cannot be used. The photochemical cyclization of butene derivatives

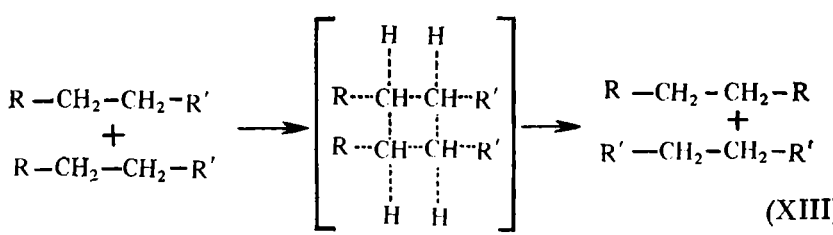
Table 54. **Thermodynamic Characteristics of the Gas-Phase Cyclization of C_3-C_5 Alkenes**

Characteristic	Value at temperature, K		
	300	500	700
Propylene → cyclopropane:			
$\Delta H°$, kJ	50.2	48.5	46.9
K_p	0	0	0
1-Butene → cyclobutane:			
$\Delta H°$, kJ	26.3	23.7	21.0
K_p	10^{-16}	10^{-12}	10^{-10}
1-Pentene → cyclopentane:			
$\Delta H°$, kJ	−56.3	−60.5	−62.3
K_p	1.1×10^7	1.1×10^3	16
Content in equilibrium mixture, fractions:			
1-pentene	0.01	0.01	0.06
cyclopentane	0.99	0.99	0.94

yielded appreciable amounts of cyclobutane derivatives [36]. This case is interesting for chemists in that it indicates the ways of seeking conditions for synthesis in situations when the thermodynamics of thermal and catalytic reactions prohibits the conducting of reactions. It is also clear that if an unstressed ring forms (a cyclopentane or cyclohexane one), the cyclization of alkenes is possible with high degrees of conversion and it will be favoured by low temperatures.

6.2. Disproportionation

Disproportionation reactions follow the scheme $2A \rightarrow B + D$, one of the products having a lower and the other a higher molecular mass than the feed stock. These bimolecular reactions have been carried out for alkanes, alkenes, and aromatics. Laboratory syntheses and industrial processes have been realized on their basis. Since A, B, and D are hydrocarbons, we can assume that an intermediate complex $[A_2]$ having a cyclic structure forms. For example, for normal alkanes, the scheme of the reaction can be as follows:

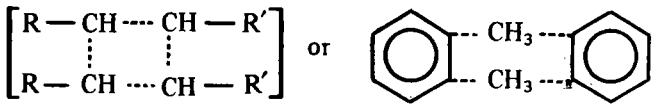


(XIII)

where R and R′ are H, CH_3, C_2H_5, etc.

If an intermediate cyclic compound contains a cyclopropane structure, methane can be one of the products.

For alkenes and aromatics, it is presumed that the intermediate formation of cyclic compounds of the type



occurs. It is quite obvious that for carrying out disproportionation reactions, the selective activation of some C—C and C—H bonds is required with the participation of a catalyst. But since these reactions have been studied relatively little, a thermodynamic analysis is needed to uncover the effective conditions of their realization.

Let us consider a disproportionation reaction following the scheme

$$2A \rightarrow B + D$$

in an ideal gas mixture. Since the number of moles does not change as a result of the reaction, we have $K_p = K_c = K_x$, and we can obtain the following equation relating the equilibrium constant K_x and the equilibrium degree of conversion y:

$$K_x = \frac{1}{4} \frac{y^2}{(1-y)^2} \tag{6.15}$$

or

$$y = \frac{4K_x - 2\sqrt{K_x}}{4K_x - 1} \tag{6.16}$$

If n parallel disproportionation reactions proceed in which one of the products, say B, is common, the scheme of the complex reaction will be as follows:

$$\begin{array}{l} \xrightarrow{K_{x_1}} A_1 + B \\ 2A \xrightarrow{K_{x_2}} A_2 + B \\ \quad \cdots \\ \xrightarrow{K_{x_n}} A_n + B \end{array} \tag{XIV}$$

Let the degree of conversion of the feed stock in the first reaction be y_1, in the second, y_2, and so on. Hence, the equilibrium amounts m_{A_i} of the reactants are as follows:

$$m_A = m_0(1 - y_1 - y_2 - \ldots - y_n) = m_0\left(1 - \sum y_i\right)$$

$$m_B = \frac{1}{2} m_0 \sum y_i, \quad m_{A_1} = \frac{1}{2} m_0 y_1, \quad m_{A_2} = \frac{1}{2} m_0 y_2, \ \ldots$$

For the equilibrium constants by Eq. (6.15), we have

$$K_{x_1}=\frac{1}{4}\,\frac{y_1\sum y_i}{(1-\sum y_i)^2}\,,\quad K_{x_2}=\frac{1}{4}\,\frac{y_2\sum y_i}{(1-\sum y_i)^2}\,,\ \ldots$$

Consequently,

$$\frac{K_{x_i}}{K_{x_1}}=\frac{y_i}{y_1}\,,\quad y_i=\frac{K_{x_i}}{K_{x_1}}\,y_1,\quad \sum y_i=\frac{\sum K_{x_i}}{K_{x_1}}\,y_1$$

and

$$K_{x_1}=\frac{\frac{1}{4}\,\frac{\sum K_{x_i}}{K_{x_1}}\,y_1^2}{\left(1-\frac{\sum K_{x_i}}{K_{x_1}}\,y_1\right)^2} \tag{6.17}$$

The positive solution of this quadratic equation has the form:

$$y_1=\frac{4\sum K_{x_i}-2\sqrt{\sum K_{x_i}}}{\frac{\sum K_{x_i}}{K_{x_1}}\left(4\sum K_{x_i}-1\right)} \tag{6.18}$$

Now it is easy to find the total degree of conversion Σy_i of the feed stock, the amount of the products B (in moles) and A_i (in moles) obtained from one mole of the charged feed stock.

6.2.1. Alkanes

The values of $\Delta H°$, K_x, and y for selected disproportionation reactions of *n*-alkanes are presented in Table 55.

A glance at the data contained in Table 55 reveals that a reaction is attended by a slight evolution of heat, and if the disproportionation products contain no methane, the heat of the reaction is close to zero. The values of K_x and y are only slightly affected by the temperature, especially if the products contain no methane, although according to thermodynamic considerations low temperatures are somewhat more favourable. The length of the feed stock carbon chain only slightly affects the values of $\Delta H°$, K_x, and y.

For normal alkanes with four or more carbon atoms, the intermediate activation of various C—C bonds is possible. The lack of equivalence, of different C—C bonds is indicated by a number of authors [40, 41].

Disproportionation reactions are catalyzed by some forms of zeolites and zeolite-containing catalysts [42], but proceed with a low selectivity owing to the occurrence of cracking, cyclization, and other reactions. The normal C_6-C_{10} alkanes yield considerable

Table 55. **Heats $\Delta H°$, Equilibrium Constants K_x, and Equilibrium Degrees of Conversion y for Selected Disproportionation Reactions of Normal Alkanes**

Reaction	Temperature, K	$\Delta H°$, kJ	K_x	y, fractions
$2C_2H_6 \rightarrow CH_4 + C_3H_8$	300	−13.4	32.7	0.92
	500	−8.8	7.1	0.84
	700	−7.9	4.0	0.80
	1000	−7.1	2.7	0.77
$2C_3H_8 \rightarrow CH_4 + n\text{-}C_5H_{12}$	300	−13.4	31.6	0.92
	500	−12.5	7.0	0.84
	700	−12.1	4.0	0.80
	1000	−11.7	2.7	0.77
$2n\text{-}C_4H_{10} \rightarrow CH_4 + n\text{-}C_7H_{16}$	300	−10.5	28.2	0.91
	500	−9.6	6.0	0.83
	700	−9.3	3.2	0.78
	1000	−9.2	2.0	0.74
$2n\text{-}C_5H_{12} \rightarrow CH_4 + n\text{-}C_9H_{20}$	300	−10.9	37.8	0.92
	500	−10.0	7.2	0.84
	700	−9.9	3.6	0.79
	1000	−9.8	2.2	0.75
$2n\text{-}C_5H_{12} \rightarrow C_2H_6 + n\text{-}C_8H_{18}$	300	−0.2	0.85	0.65
	500	−0.2	0.85	0.65
	700	−0.4	0.84	0.65
	1000	−0.7	0.82	0.64
$2n\text{-}C_6H_{14} \rightarrow C_2H_6 + n\text{-}C_{10}H_{22}$	300	−0.1	0.70	0.62
	500	−0.1	0.70	0.62
	700	−0.2	0.70	0.62
	1000	−0.4	0.68	0.62
$2n\text{-}C_5H_{12} \rightarrow n\text{-}C_4H_{10} + n\text{-}C_6H_{14}$	300	−0.5	1.31	0.70
	500	−0.5	1.20	0.69
	700	−0.4	1.18	0.68
	1000	−0.4	1.16	0.68

amounts of methane, butane, and isobutane, and also high-molecular saturated compounds. This is consistent to a certain extent with the data of thermodynamic analysis (see Table 55) from which it follows that methane and butane can be the most probable products of disproportionation, but not ethane (see the values of the equilibrium constant).

If disproportionation can proceed in several directions (a complex reaction), the equilibrium degree of conversion will be higher than for one reversible reaction according to the data of Table 55. The calculations for this case are given at the beginning of Sec. 6.2.

6.2.2. Alkenes

Of the greatest technical significance is the disproportionation of propylene with the formation of ethylene and *n*-butene, chiefly one of the 2-butenes. But if the catalyst activates the migration of

the double bond, 1-butene can also be a product. Table 56 gives the values of $\Delta H°$, K_x, and y for the disproportionation of propylene with the formation of ethylene and various *n*-butenes, and also the thermodynamic characteristics of the reactions of disproportionation of C_4 and C_5 alkenes.

Table 56. **Heats $\Delta H°$, Equilibrium Constants K_x, and Equilibrium Degrees of Conversion y for Disproportionation Reactions of Alkenes**

Reaction	Temperature, K	$\Delta H°$, kJ	K_x	y, fractions
$2C_3H_6 \rightarrow C_2H_4 +$ *cis*-2-butene	300	4.5	0.033	0.26
	500	3.7	0.062	0.33
	700	3.5	0.078	0.37
	1000	1.8	0.092	0.38
$2C_3H_6 \rightarrow C_2H_4 +$ *trans*-2-butene	300	0.2	0.104	0.39
	500	0.6	0.112	0.40
	700	1.4	0.121	0.41
	1000	1.7	0.131	0.42
$2C_3H_6 \rightarrow C_2H_4 +$ 1-butene	300	11.4	0.0034	0.10
	500	12.0	0.018	0.21
	700	12.7	0.048	0.30
	1000	13.4	0.106	0.39
2 (*iso*-C_4H_8) $\rightarrow C_2H_4 +$ 2,3-dimethyl-2-butene	300	19.6	0.0002	0.03
	500	18.1	0.004	0.12
	700	17.2	0.015	0.19
	1000	16.9	0.036	0.27
2 (*cis*-2-Pentene) $\rightarrow$ *cis*-2-butene + *cis*-3-hexene	300	0.7	0.17	0.45
	500	0.4	0.17	0.45
	700	0.4	0.19	0.46
	1000	−1.0	0.20	0.47
2 (*n*-1-Butene) $\rightarrow C_2H_4 +$ *n*-1-hexene	300	10.9	0.0059	0.13
	500	11.7	0.034	0.27
	700	12.1	0.083	0.37
	1000	13.0	0.14	0.43
2 (*n*-1-Pentene) $\rightarrow C_2H_4 +$ *n*-1-octene	300	11.3	0.0037	0.11
	500	11.7	0.025	0.24
	700	12.1	0.055	0.32
	1000	13.0	0.093	0.38

It can be seen from Table 56 that the disproportionation of alkenes proceeds with a slight absorption of heat. Therefore, the equilibrium constants and the equilibrium degrees of conversion grow somewhat with increasing temperature.

For various simple disproportionation reactions of propylene, the degrees of conversion even at 1000 K do not exceed 42%. At low temperatures, the formation of *trans*-2-butene, and then of *cis*-2-butene and 1-butene is most probable. At elevated temperatures, the various *n*-butenes form with about the same probability. One must bear in mind, however, that if several isomer *n*-butenes form in a real

process (a complex disproportionation reaction), the conversion of the feed stock will be somewhat higher than that indicated in Table 56. Thus, if ethylene (B) and three normal butenes (A_1, A_2, and A_3) form from propylene (A), i.e. the reaction follows the scheme

$$2A \begin{cases} \xrightarrow{K_{x_1}} B + A_1 \\ \xrightarrow{K_{x_2}} B + A_2 \\ \xrightarrow{K_{x_3}} B + A_3 \end{cases} \qquad \text{(XV)}$$

and the degrees of conversion in each direction are y_1, y_2, and y_3, respectively, we have:

$$K_{x_1} = \frac{1}{4}\,\frac{y_1(y_1+y_2+y_3)}{(1-y_1-y_2-y_3)^2}, \quad K_{x_2} = \frac{1}{4}\,\frac{y_2(y_1+y_2+y_3)}{(1-y_1-y_2-y_3)^2}$$

$$K_{x_3} = \frac{1}{4}\,\frac{y_3(y_1+y_2+y_3)}{(1-y_1-y_2-y_3)^2}$$

Consequently,

$$y_2 = \frac{K_{x_2}}{K_{x_1}}\,y_1, \qquad y_3 = \frac{K_{x_3}}{K_{x_1}}\,y_1$$

and

$$K_{x_1} = \frac{\frac{1}{4}\,y_1\left(y_1 + \frac{K_{x_2}}{K_{x_1}}\,y_1 + \frac{K_{x_3}}{K_{x_1}}\,y_1\right)}{\left(1 - y_1 - \frac{K_{x_2}}{K_{x_1}}\,y_1 - \frac{K_{x_3}}{K_{x_1}}\,y_1\right)^2} = \frac{\frac{1}{4}\,y_1^2\left(1 + \frac{K_{x_2}}{K_{x_1}} + \frac{K_{x_3}}{K_{x_1}}\right)}{\left[1 - \left(1 + \frac{K_{x_2}}{K_{x_1}} + \frac{K_{x_3}}{K_{x_1}}\right)y_1\right]^2}.$$

For n parallel reactions of disproportionation with the formation of ethylene, we obtain

$$y_i = \frac{K_{x_i}}{K_{x_1}}; \quad K_{x_1} = \frac{\frac{1}{4}\,y_1^2\left(\sum\limits_{i=1}^{n} K_{x_i}/K_{x_1}\right)}{\left[1 - \left(\sum\limits_{i=1}^{n} K_{x_i}/K_{x_1}\right)y_1\right]^2}$$

For example, for the disproportionation of propylene at 300 K in accordance with Table 56, we have $K_{x_1} = 0.033$, $K_{x_2} = 0.104$, $K_{x_3} = 0.0034$, hence $\sum K_{x_i}/K_{x_1} = 0.1404/0.033 = 4.255$, and by formula (6.17), we have

$$0.033 = \frac{\frac{1}{4}\,y_1^2 \times 4.255}{(1 - 4.255y_1)^2}$$

The solution of this quadratic equation is $y_1 = 0.104$. Therefore, using the formula $y_i = (K_{x_i}/K_{x_1})\, y_1$, we find $y_2 = (0.104/0.033) \times \times 0.104 = 0.328$ and $y_3 = (0.0034/0.033) \times 0.104 = 0.011$. The overall degree of conversion when the three reactions proceed will be about $0.44 = 44\%$, whereas by the simple reaction, the maximum conversion was 0.39.

Consequently, when comparing calculated and experimental data, one must have in view what isomer *n*-butenes are contained in the reaction mixture.

Inspection of the data in Table 56 reveals that the most appreciable growth in the conversion is observed when the temperature is elevated to 700 K, hence the further elevation of the temperature is less effective from thermodynamic considerations. But in the realization of disproportionation reactions, the kinetic data are of the greatest importance. Therefore, to avoid the proceeding of undesirable side cracking reactions and to ensure a high selectivity, the industrial process of propylene disproportionation (what is called the triolefin process) is carried out at relatively low (60-250 °C) temperatures and high volume rates (15-150 h^{-1}) of introducing the feed stock. This makes it possible to obtain disproportionation products with a selectivity exceeding 90%.

In the disproportionation of a skeleton isomer, the heat of the reaction will be higher and the equilibrium constant and conversion somewhat lower than in the disproportionation of a normal 1-alkene.

With an increase in the molecular mass of the alkene in a reaction of one type (the feed stock and products are normal 1-alkenes), the heat of the reaction does not virtually change, while K_x and y are the largest for C_4 alkenes.

It can be seen from Table 56 that the disproportionation of alkenes with an inner double bond proceeds with very low heat effects and comparatively high conversions (45-47%). For these reactions, the temperature affects K_x and y very slightly.

Disproportionation of Alkenes with the Redistribution of Hydrogen. Hydrogen redistribution reactions proceed like side ones in thermal and catalytic processes of hydrocarbon treatment. In particular, they result in the formation of carbonaceous deposits lean in hydrogen. The role of alkenes in the formation of such deposits has been noted repeatedly because unsaturated hydrocarbons form in various processes of treatment of hydrocarbon feed stock. It is therefore interesting to determine the possibility of their disproportionation with the retaining of the number of carbon atoms in the feed stock and product molecules and the redistribution of only the hydrogen atoms.

For example, ethane and acetylene can be produced from ethylene as a result of the redistribution of the hydrogen. Although such a reaction can be considered as a complex one consisting of two

simple ones, namely, hydrogenation and dehydrogenation, it can also proceed in the absence of hydrogen in the reaction medium, i.e. like a simple reaction. Not only alkynes (the acetylene series), but also dienes can be produced from alkenes with three or more carbon atoms as a result of hydrogen redistribution.

For analysing the thermodynamic probability of hydrogen redistribution, Table 57 presents the equilibrium constants for the reactions of normal 1-alkenes with the formation of alkynes and dienes.

Table 57. **Equilibrium Constants for the Reactions of Normal 1-Alkenes at 300-1500 K in the Gas Phase at Moderate Pressures Yielding Alkynes and Dienes**

Reaction	Equilibrium constant $K_p = K_x$ at temperature, K			
	500	700	1100	1500
$2C_2H_4 \rightarrow C_2H_2 + C_2H_6$	10^{-7}	10^{-3}	0.01	0.03
$2C_3H_6 \rightarrow$ propyne + propane	10^{-8}	10^{-4}	$10^{-2.6}$	0.01
$2C_4H_8 \rightarrow$ butyne + *n*-butane	10^{-7}	10^{-3}	0.01	0.01
$2C_5H_{10} \rightarrow$ pentyne + *n*-pentane	$10^{-7.5}$	$10^{-3.5}$	0.01	0.01
$2C_3H_6 \rightarrow$ propadiene + propane	10^{-9}	$10^{-4.5}$	10^{-3}	$10^{-2.5}$
$2C_4H_8 \rightarrow$ 1,3-butadiene + *n*-butane	17	1.6	0.6	0.3
$2C_5H_{10} \rightarrow$ *cis*-1,3-pentadiene + *n*-pentane	$10^{3.6}$	12	1.9	0.7

It can be seen from the table that the redistribution of hydrogen in alkenes with the formation of alkynes or cumulated dienes will not occur at temperatures below 700 K and even at high temperatures can involve only a small part of the feed stock.

However, the redistribution of hydrogen with the formation of conjugated dienes for alkenes with four or more carbon atoms is very probable thermodynamically. It may proceed virtually completely at low temperatures, and although the equilibrium constants decrease, even at 1500 K the conversion of the feed stock by about 50% is possible.

These conclusions are supported by the data on the hydrocarbon cracking and pyrolysis products obtained in experimental compositions. In cracking processes conducted at temperatures of 550 °C and below, no alkynes or cumulated dienes form, but small (because of kinetic and not thermodynamic restrictions) amounts of conjugated dienes are obtained. The products of high-temperature pyrolysis contain substantial amounts of 1,3-dienes, and appreciable amounts of acetylene and propadiene (allene) appear. This is why the formation from alkenes of products lean in hydrogen via conjugated dienes is probable thermodynamically.

Table 58. **Heats $\Delta H°$, Equilibrium Constants K_x, and Equilibrium Degrees of Conversion y for Methylcyclopentane ($C_5H_9CH_3$) and Methylcyclohexane ($C_6H_{11}CH_3$) Disproportionation Reactions**

Reaction	Temperature, K	$\Delta H°$, kJ	K_x	y, fractions
$2C_5H_9CH_3 \rightarrow C_5H_{10} + C_5H_8(CH_3)_2$ (cyclopentane) (1,1-dimethylcyclopentane)	300	−2.5	0.086	0.37
	500	−2.5	0.058	0.33
	700	−2.2	0.048	0.31
	1000	−1.4	0.044	0.29
$2C_5H_9CH_3 \rightarrow C_5H_{10} + C_5H_8(CH_3)_2$ (*cis*-1,2-dimethylcyclopentane)	300	6.6	0.0059	0.12
	500	6.6	0.017	0.20
	700	6.5	0.025	0.24
	1000	6.5	0.036	0.27
$2C_5H_9CH_3 \rightarrow C_5H_{10} + C_5H_8(CH_3)_2$ (*trans*-1,2-dimethylcyclopentane)	300	−0.8	0.111	0.40
	500	−0.8	0.100	0.39
	700	−0.7	0.094	0.38
	1000	−0.3	0.092	0.37
$2C_5H_9CH_3 \rightarrow C_5H_{10} + C_5H_8(CH_3)_2$ (*cis*-1,3-dimethylcyclopentane)	300	2.4	0.032	0.26
	500	2.4	0.047	0.30
	700	2.4	0.055	0.32
	1000	2.8	0.064	0.34
$2C_5H_9CH_3 \rightarrow C_5H_{10} + C_5H_8(CH_3)_2$ (*trans*-1,3-dimethylcyclopentane)	300	0.2	0.080	0.36
	500	0.2	0.081	0.36
	700	0.2	0.081	0.36
	1000	0.5	0.084	0.37
$2C_5H_9CH_3 \rightarrow C_5H_{10} + C_5H_9C_2H_5$ (ethylcyclopentane)	300	9.0	0.0092	0.16
	500	8.2	0.042	0.29
	700	7.5	0.077	0.35
	1000	7.1	0.112	0.40
$2C_6H_{11}CH_3 \rightarrow C_6H_{12} + C_6H_{10}(CH_3)_2$ (methylcyclohexane) (cyclohexane) (1,1-dimethylcyclohexane)	300	5.4	0.0069	0.14
	500	3.6	0.015	0.19
	700	2.9	0.018	0.20
	1000	2.9	0.021	0.22
$2C_6H_{11}CH_3 \rightarrow C_6H_{12} + C_6H_{10}(CH_3)_2$ (*cis*-1,2-dimethylcyclohexane)	300	14.2	0.0006	0.05
	500	12.8	0.0054	0.12
	700	11.8	0.013	0.18
	1000	11.2	0.023	0.23
$2C_6H_{11}CH_3 \rightarrow C_6H_{12} + C_6H_{10}(CH_3)_2$ (*trans*-1,2-dimethylcyclohexane)	300	6.4	0.0095	0.16
	500	5.7	0.025	0.23
	700	5.1	0.035	0.27
	1000	5.0	0.046	0.30
$2C_6H_{11}CH_3 \rightarrow C_6H_{12} + C_6H_{10}(CH_3)_2$ (*cis*-1,3-dimethylcyclohexane)	300	1.6	0.06	0.33
	500	0.2	0.07	0.34
	700	−0.4	0.07	0.34
	1000	−0.5	0.07	0.33
$2C_6H_{11}CH_3 \rightarrow C_6H_{12} + C_6H_{10}(CH_3)_2$ (*trans*-1,3-dimethylcyclohexane)	300	9.8	0.0045	0.11
	500	8.6	0.020	0.22
	700	7.2	0.033	0.26
	1000	6.2	0.048	0.31
$2C_6H_{11}CH_3 \rightarrow C_6H_{12} + C_6H_{10}(CH_3)_2$ (*cis*-1,4-dimethylcyclohexane)	300	9.8	0.0023	0.08
	500	8.6	0.010	0.16
	700	7.2	0.018	0.20
	1000	6.2	0.024	0.23

Table 58 (*concluded*)

Reaction	Temperature, K	ΔH°, kJ	K_x	y, fractions
$2C_6H_{11}CH_3 \rightarrow C_6H_{12} + C_6H_{11}C_2H_5$ (ethylcyclohexane)	300	14.6	0.0014	0.11
	500	13.9	0.014	0.18
	700	12.8	0.033	0.26
	1000	12.2	0.063	0.33

6.2.3. Five- and Six-Membered Cycloalkanes

The disproportionation of alkyl-substituted cycloalkanes produces an unsubstituted and a disubstituted cycloalkane:

Methylcyclopentane $\longrightarrow$ Cyclopentane + Dimethylcyclopentane
Methylcyclohexane $\longrightarrow$ Cyclohexane + Dimethylcyclohexane

If these reactions are actually realized in real processes, they occur only as side ones. Nevertheless, their thermodynamic analysis is helpful when studying the transformations of hydrocarbons. Table 58 presents the thermodynamic characteristics of methylcyclopentane and methylcyclohexane disproportionation reactions.

It can be seen from the data in Table 58 that the disproportionation of cycloalkanes proceeds with small heat effects. Here depending on the structure of the dialkyl-substituted compound and the temperature, both the absorption and evolution of heat are possible. The conversion of the feed stock in simple reactions does not exceed 40%.

The formation of hem-substituted compounds and *trans*-isomers is most probable thermodynamically at low temperatures; at high temperatures, the different isomers form with a close probability. This is consistent with the data on the isomerization of cycloalkanes (see Sec. 6.1).

6.2.4. Alkylbenzenes

The disproportionation of toluene with the obtaining of benzene and one or several xylenes is carried out as the target or side reaction in a number of processes. Let us consider the thermodynamic characteristics of this reaction (Table 59).

Examination of the data given in Table 59 on the heats and equilibrium constants reveals that these quantities change only slightly with the temperature. The heats of producing xylenes are very low and depending on the reaction temperature can be both positive and negative. Owing to the closeness of the heats of the reactions to zero, the temperature also affects only insignificantly the equilibrium constants and, consequently, the equilibrium composition.

Table 59. **Heats $\Delta H°$ (in kJ) and Equilibrium Constants K_x for Disproportionation Reactions of Aromatics in an Ideal Gas Phase**

Reaction and thermodynamic quantities	Temperature, K							
	300	400	500	600	700	800	900	1000
2 (Toluene) → benzene + *m*-xylene								
$\Delta H°$	0.4	0.2	0.03	−0.3	−1.0	−1.6	−2.4	−3.3
K_x	0.16	0.17	0.17	0.17	0.17	0.16	0.16	0.15
2 (Toluene) → benzene + *o*-xylene								
$\Delta H°$	1.9	2.5	2.6	2.5	2.0	1.5	0.8	0
K_x	0.045	0.056	0.075	0.075	0.078	0.081	0.082	0.083
2 (Toluene) → benzene + *p*-xylene								
$\Delta H°$	0.8	0.9	0.5	0	−0.8	−1.6	−2.5	−3.4
K_x	0.066	0.072	0.075	0.076	0.075	0.073	0.070	0.068
2 (Toluene) → benzene + ethylbenzene								
$\Delta H°$	12.7	13.0	13.2	13.2	13.0	12.6	12.1	11.5
K_x	0.0015	0.0054	0.012	0.020	0.029	0.038	0.047	0.055
2 (*m*-Xylene) → toluene + 1,2,3-trimethylbenzene								
$\Delta H°$	6.0	6.1	6.3	6.4	6.5	6.7	6.8	7.2
K_x	0.028	0.052	0.075	0.096	0.12	0.13	0.15	0.16
2 (*m*-Xylene) → toluene + 1,2,4-trimethylbenzene								
$\Delta H°$	1.6	1.8	2.0	2.1	2.4	2.7	4.0	4.3
K_x	0.60	0.711	0.80	0.86	0.92	0.97	1.02	1.06
2 (*m*-Xylene) → toluene + 1,3,5-trimethylbenzene								
$\Delta H°$	−0.6	−0.7	−0.7	−0.6	−0.4	−0.2	0.05	0.5
K_x	0.4	0.38	0.36	0.35	0.35	0.35	0.35	0.35

The formation of *m*-xylene has the highest thermodynamic probability. At low temperatures, the ratio of *o*-xylene to *p*-xylene in the products will exceed unity, and at high ones it will be less than unity. Ethylbenzene can be contained in appreciable amounts in the disproportionation products only at high temperatures. The heat of its formation is positive, and although it is higher in magnitude than that of xylenes, this reaction also proceeds with the slight absorption of heat. If toluene yields benzene and only *m*-xylene, the equilibrium degree of conversion of the feed stock will be within 44-45% in the temperature range of 300-1000 °C, and the composition of the equilibrium mixture will be (in mole fractions): toluene—0.56, benzene—0.22, and *m*-xylene—0.22 (the formulas for calculations are given at the beginning of this section).

Table 60. **Composition of Equilibrium Mixture (in Mole Fractions) and Degree of Conversion (in %) in the Disproportionation of Toluene in an Ideal Gas Mixture with the Simultaneous Formation of C_8 Alkylbenzenes**

Composition of equilibrium mixture	Temperature, K							
	300	400	500	600	700	800	900	1000
Benzene and three xylene isomers:								
toluene	0.49	0.47	0.46	0.46	0.47	0.47	0.47	0.47
benzene	0.255	0.265	0.267	0.267	0.265	0.265	0.265	0.265
m-xylene	0.15	0.15	0.15	0.15	0.14	0.14	0.14	0.14
o-xylene	0.045	0.05	0.058	0.058	0.065	0.065	0.065	0.065
p-xylene	0.06	0.065	0.065	0.065	0.06	0.06	0.06	0.06
degree of conversion	51	53	53.5	53.5	53	53	53	53
Benzene and all C_8 alkylbenzenes:								
toluene	0.49	0.48	0.46	0.46	0.46	0.46	0.46	0.46
benzene	0.25	0.26	0.27	0.27	0.27	0.27	0.27	0.27
m-xylene	0.15	0.145	0.14	0.135	0.13	0.125	0.12	0.11
o-xylene	0.045	0.05	0.06	0.06	0.06	0.06	0.06	0.065
p-xylene	0.06	0.06	0.06	0.06	0.06	0.055	0.055	0.055
ethylbenzene	0.005	0.005	0.01	0.015	0.02	0.03	0.035	0.04
degree of conversion	51	52	54	54	54	54	54	54

Disproportionation catalysts, however, also activate the isomerization of xylenes, therefore thermodynamic calculations taking into account the proceeding of parallel reactions are needed. If the three xylene isomers form simultaneously, the degree of conversion of toluene increases to 51-53%. When the possibility of the formation of ethylbenzene is also taken into consideration, this value changes by not over 1% (Table 60).

A close look at the data in Table 60 reveals that one should not attempt to produce ethylbenzene from toluene. In disproportionation of the latter, only xylenes can be obtained in appreciable amounts, *m*-xylene occupying first place among them. Owing to the very slight influence of the temperature on the equilibrium composition, the choice of the disproportionation conditions is determined only by kinetic factors. If one or two xylene isomers are obtained in disproportionation, thermodynamic calculations should be performed for the actually obtained substances using data on the equilibrium constants (see Table 59). In most real situations, all three xylene isomers are produced, and the data of Table 60 can be used.

In connection with the growing interest in the production of tri- and tetramethylbenzenes, it will be expedient to estimate the thermodynamic possibility of preparing them by disproportionation. For example, trimethylbenzene can be produced from the least scarce of the xylenes—*m*-xylene—by the reaction

$$2(m\text{-xylene}) \rightarrow \text{toluene} + \text{trimethylbenzene}$$

It is naturally necessary to establish the extent of such a reaction and what amounts and which trimethylbenzenes can be obtained. In this connection, we have performed thermodynamic calculations whose results are given in Table 61.

It can be seen from the data of Tables 59 and 61 that the heats of disproportionation are not large and depending on the structure of the trimethylbenzene and the temperature can be both positive and negative. The disproportionation of *m*-xylene proceeds with larger degrees of conversion than of toluene, i.e. with an increase in the number of alkyl substituents, the possible extent of disproportionation increases. Both at low and high temperatures, 1,2,4-trimethylbenzene is the main product of disproportionation, elevation of the temperature increasing the selectivity of its formation. Appreciable amounts of 1,3,5-trimethylbenzene can also be obtained, especially at low temperatures.

6.2.5. Formation of Coke

The formation of coke can be considered as disproportionation of hydrocarbons with the simultaneous redistribution of the carbon and hydrogen. It should not be identified with the decomposition

Table 61. **Composition of Equilibrium Mixture (in Mole Fractions) and Degree of Conversion (in %) of *m*-Xylene with the Simultaneous Formation of Trimethylbenzenes**

Composition of equilibrium mixture	Temperature, K							
	300	400	500	600	700	800	900	1000
m-Xylene	0.34	0.325	0.31	0.31	0.29	0.29	0.29	0.28
Toluene	0.33	0.33	0.345	0.345	0.355	0.355	0.355	0.365
1,2,3-Trimethylbenzene	0.01	0.015	0.02	0.025	0.03	0.030	0.035	0.035
1,2,4-Trimethylbenzene	0.19	0.21	0.225	0.23	0.235	0.235	0.24	0.24
1,3,5-Trimethylbenzene	0.13	0.12	0.10	0.09	0.09	0.09	0.08	0.08
Degree of conversion	66	67.5	69	69	71	71	71	72

into simple substances because hydrogen is usually not the only light product of coking.

Coke may be either the target or a side product of petroleum processing. Depending on the nature of the feed stock and the process conditions, the C:H ratio in the coke varies from 1:0.8 (primary coke) to 1:0.24 (roasted coke). It should be noted that a structure with two condensed benzene nuclei corresponds to the chemical composition $CH_{0.6}$, and a structure with 20 or more condensed benzene nuclei—to $CH_{0.24}$. Coke forms in the largest amounts from aromatics lean in hydrogen, but since cyclization proceeds in the processing of any hydrocarbons, coke can be produced from saturated hydrocarbons and alkenes or their derivatives. In the formation of coke, owing to disproportionation, hydrocarbons with a molecular mass lower than that of the feed stock, what we call the light-end products, and sometimes hydrogen are also obtained.

To perform thermodynamic calculations, one must establish the thermodynamic functions of coke. Data on these functions are generally not contained in the literature because coke is assumed to be characterized by the same functions as graphite. This assumption leads to substantial errors.

Thermodynamic Functions of Coke. To determine the thermodynamic functions of coke having the composition CH_a, we interpolate the data for graphite (CH_0) and polycyclic aromatics. For this purpose, from the known values of C_p°, S°, ΔH_f°, and ΔG_f° for graphite and solid polycyclic hydrocarbons (naphthalene, anthracene, triphenylmethane), we find the thermodynamic function Φ reduced to the CH_a group, and then find its dependence on a. The relevant values are presented in Table 62.

The data of Table 62 reveal a trend of diminishing of the values of the thermodynamic functions (per CH_a group) with a decreasing hydrogen content.

Table 62. **Thermodynamic Functions of Graphite and Selected Polycyclic Hydrocarbons**

Substance	Amount, mol	Thermodynamic function			
		$C_{p,298}^\circ$, J/K	S_{298}°, J/K	$\Delta H_{f,298}^\circ$, J	$\Delta G_{f,298}^\circ$, kJ
Graphite (CH_0)	1	8.7	5.7	0	0
Anthracene $C_{14}H_{10}$	1	207.9	207.5	106.8	263.4
($CH_{0.7}$)	1/14	14.9	14.8	7.6	18.8
Naphthalene $C_{10}H_8$	1	165.7	167.8	78.5	201.3
($CH_{0.8}$)	1/10	16.6	16.8	7.8	20.1
Triphenylmethane $C_{19}H_{16}$	1	295.0	312.1	161.9	412.5
($CH_{0.84}$)	1/19	15.5	16.4	8.5	21.7

If we use linear interpolation as a first approximation and let Φ stand for a thermodynamic function of a solid carbon compound of the formula CH_a (where $a \leqslant 0.9$) with an arbitrary value of a, Φ_1 stand for its value for graphite ($a = 0$), and Φ_2 for its value for anthracene ($a = 0.7$), we have

$$\frac{\Phi - \Phi_1}{\Phi_2 - \Phi_1} = \frac{a}{0.7}$$

or

$$\Phi = \Phi_1 + \frac{\Phi_2 - \Phi_1}{0.7} a \tag{6.19}$$

Hence, we find for coke the formula CH_a for a mass of $(12 + a)$ grammes:

$$C^\circ_{p,298} = 8.7 + 8.86a \text{ J/K} \tag{6.20}$$

$$S^\circ_{298} = 5.7 + 13.0a \text{ J/K} \tag{6.21}$$

$$\Delta H^\circ_{f,298} = 10.86a \text{ kJ/K} \tag{6.22}$$

$$\Delta G^\circ_{f,298} = 26.86a \text{ kJ/K} \tag{6.23}$$

Linear interpolation gives a satisfactory coincidence with the tabulated values for the above and some other substances. To calculate the thermodynamic functions of coke for elevated temperatures, we can employ approximate relations based on the condition that $C^\circ_{pT} = \text{const}_1$ and $\Delta C^\circ_{pT} = \text{const}_2$, which increases the error of the calculations only insignificantly. This results in the following relations for the enthalpy and Gibbs energy of formation of coke (in kJ):

$$\Delta H^\circ_{f,T} = a\,[10.86 - 5.5 \times 10^{-3}(T - 298)] \tag{6.24}$$

$$\Delta G^\circ_{f,T} = a\left[10.86 - 5.5 \times 10^{-3}\left(T - 298 - \ln\frac{T}{298}\right) + 53.7 \times 10^{-3}T\right] \tag{6.25}$$

Table 63 gives the enthalpies and Gibbs energies of formation of coke.

Reactions of Coke Formation from Individual Hydrocarbons. Assume that primary coke of the composition CH_a forms from the hydrocarbon C_nH_m. Simultaneously, the light-end product of the composition $C_{n_1}H_{m_1}$ and, possibly, hydrogen are produced. Hence, the reaction of coking can be written in the form

$$C_nH_m \rightarrow \nu_{le}C_{n_1}H_{m_1} + \nu_h H_2 + \nu_c CH_a \tag{XVI}$$

where ν_{le}, ν_h, and ν_c are the molar yields of the light-end product, hydrogen, and coke, respectively.

It follows from the equations of the balance of the carbon and hydrogen atoms that

$$n = \nu_{le}n_1 + \nu_c, \quad m = \nu_{le}m_1 + 2\nu_h + \nu_c a$$

Table 63. **Standard Enthalpies ΔH_f° (in kJ) and Gibbs Energies ΔG_f° (in kJ) of Coke Formation Reduced to the Group CH_a [i.e. to $(12+a)$ Grammes]***

Temperature, K	Thermodynamic function	Composition of coke (CH_a)				
		$CH_{0.2}$	$CH_{0.4}$	$CH_{0.6}$	$CH_{0.8}$	CH
300	ΔH_f°	2.2	4.3	6.5	8.7	10.8
	ΔG_f°	5.6	11.2	16.8	22.4	28.0
400	ΔH_f°	2.1	4.1	6.2	8.2	10.3
	ΔG_f°	6.5	13.0	19.5	25.9	32.4
500	ΔH_f°	1.9	3.9	5.8	7.8	9.7
	ΔG_f°	7.6	15.2	22.8	30.4	38.0
600	ΔH_f°	1.8	3.7	5.5	7.4	9.2
	ΔG_f°	8.7	17.5	26.2	35.0	43.7
700	ΔH_f°	1.7	3.5	5.2	6.9	8.6
	ΔG_f°	9.9	19.8	29.7	39.6	49.5
800	ΔH_f°	1.6	3.2	4.9	6.5	8.1
	ΔG_f°	11.1	22.2	33.2	44.3	55.4
1000	ΔH_f°	1.4	2.8	4.2	5.6	7.0
	ΔG_f°	13.5	26.9	40.4	53.9	67.4
1200	ΔH_f°	1.2	2.4	3.5	4.7	5.9
	ΔG_f°	15.9	31.8	47.7	63.6	79.5

* For graphite ($a = 0$), both ΔH_f° and ΔG_f° equal zero.

If the type of the light-end product structure is known, n_1 and m_1 can be related by the expression

$$m_1 = \alpha n_1 + \beta$$

where α and β are preset numbers, for example, for alkanes $\alpha = \beta = 2$ and for alkenes $\alpha = 2$, $\beta = 0$.

By using the above expressions, we can simplify our estimate of the quantities ν_{le}, ν_h, n_1, and m_1, which are needed to compile the coking equation. Thus, it follows from them that when $\beta \neq 0$, we have:

$$\nu_{le} = \frac{m - \alpha n - 2\nu_h - (\alpha - a)\nu_c}{\beta}, \quad n_1 = \frac{n - \nu_c}{\nu_{le}}, \quad m_1 = \alpha n_1 + \beta$$

If $\beta = 0$, we can find only the product $\nu_{le} n_1 = n - \nu_c$.

It is assumed that the values of ν_h and ν_c are estimated from experimental data.

Below we give some possible equations of model reactions of coke formation (Table 64) from the alkane *n*-hexane (reactions 1-3), the

Table 64. **Model Reactions of Coke Formation**

Reaction No.	Reaction*	Coke yield, mass fractions	Type of light-end product
1	$C_6H_{14} \rightarrow 1.15C_5H_{12} + 0.34CH_{0.8}$	0.05	Alkane
2	$C_6H_{14} \rightarrow 1.33C_4H_{10} + 0.68CH_{0.8} + 0.8H_2$	0.10	Alkane
3	$C_6H_{14} \rightarrow 1.32C_2H_4 + 3.36CH_{0.8} + 3.01H_2$	0.50	Alkene
4	$C_6H_{14} \rightarrow 0.66C_4H_6 + 3.36CH_{0.8} + 3.68H_2$	0.50	Diene
5	$C_6H_{12} \rightarrow 1.36C_2H_4 + 3.28CH_{0.8} + 2.97H_2$	0.50	Alkene
6	$C_6H_6 \rightarrow 1.48C_2H_4 + 3.04CH_{0.8} + 2.82H_2$	0.50	Alkene

* The coefficients ν have been rounded off.

alkene *n*-1-hexene (reaction 5), the cycloalkane cyclohexane (reaction 4) and the aromatic benzene (reaction 6) and also the enthalpies and Gibbs energies of these reactions (Table 65).

Table 65. **Enthalpies and Gibbs Energies of Reactions of Decomposition of Individual Hydrocarbons into Simple Substances (Graphite, Hydrogen) and of the Model Coking Reactions Given in Table 64 for Temperatures of 300, 500, and 1000 K**

Reaction	ΔH° (kJ) at T, K			ΔG° (kJ) at T, K		
	300	500	1000	300	500	1000
$C_6H_{14} \rightarrow 6C + 7H_2$	167.4	186.1	206.1	−0.8	−118.5	−433.3
1*	1.8	1.4	2.0	−2.1	−4.7	−9.9
2*	5.3	4.9	2.7	−8.1	−16.8	−37.7
3*	266	274	276	161	90	−96
4*	267	280	288	54	−29	−261
C_6H_{12}** $\rightarrow 6C + 6H_2$	41.8	57.6	75.3	−88.2	−180.0	−425.9
5*	141.4	146.0	146.1	74.9	29.5	−88.5
$C_6H_6 \rightarrow 6C + 3H_2$	−82.8	−73.4	−62.0	−130.0	−164.0	−260.0
6*	21.1	20.3	12.0	36.3	47.3	78.3
$C_2H_2 \rightarrow 2C + H_2$	−226.7	−226.1	−223.0	−209.0	−197.0	−170.0

* The number of the reaction in Table 64.
** Normal 1-hexene.

Inspection of the data of Table 65 shows that coking is promoted by high temperatures. For example, reactions 3 and 5 become thermodynamically possible only close to 1000 K, while at 300-500 K they do not virtually proceed. The formation of coke from aliphatic

hydrocarbons at high temperatures may be attended by the formation of a light-end product of any structure (alkane, alkene, diene). An aromatic forms coke owing to polycondensation with the evolution of hydrogen. The reaction of producing coke from benzene (reaction 5) with the simultaneous separation of a light-end aliphatic hydrocarbon is thermodynamically improbable.

It can also be seen that the disproportionation of alkanes becomes the more probable, the larger the amount of coke formed and the smaller the molecular mass of the light-end product (reactions 1 and 2). Consequently, the evolution of substantial amounts of methane and hydrogen in coking can be explained by thermodynamic considerations. The formation in the light-end product of dienes (reaction 4) becomes just as probable thermodynamically at high temperatures, which is consistent with experimental data.

The formation of coke from alkanes, alkenes, and cycloalkanes is generally an endothermic reaction, and from aromatics and alkynes is an exothermic one.

When determining the composition of the equilibrium mixture for a coke-formation reaction, one must remember that the equilibrium constant K_p evaluated by the equation of an isotherm is expressed in terms of the partial pressures of only the gaseous products. Thus, for the reaction of a hydrocarbon C_nH_m (see above), we have

$$K_p = \frac{p_{C_{n_1}H_{m_1}}^{\nu_{le}} p_{H_2}^{\nu_{H_2}}}{p_{C_nH_m}} \tag{6.26}$$

For example, for reaction 3, the following holds:

for 500 K

$$K_{p,500}^{\circ} = \exp\left(-\frac{90\,000}{8.31 \times 500}\right) = e^{-21.7}$$

for 1000 K

$$K_{p,1000}^{\circ} = \exp\left(\frac{96\,000}{8.31 \times 1000}\right) = e^{11.6}$$

At 500 K, the reaction does not practically proceed, while at 1000 K from the condition

$$e^{11.6} = \frac{p_{C_2H_4}^{1.32} p_{H_2}^{3.01}}{p_{C_6H_{14}}} (p^{\circ})^{-3.32}$$

it follows that at pressures below 1 MPa the achieved degree of conversion will exceed 90%.

Influence of Dilution with Hydrogen and the Total Pressure on the Equilibrium Conversion in Coking. The higher the hydrogen pressure, the lower will be the degree of conversion of the feed stock and the amount of coke formed. This is an important result because it shows

that when processing petroleum under the pressure of hydrogen, the amount of coke formed decreases not only because of kinetic, but also because of thermodynamic restrictions. In this connection, we shall give an expression for calculating the degree of conversion of the feed stock in a coke-formation reaction conducted with dilution of the feed stock with hydrogen.

Let y be the degree of conversion of the hydrocarbon C_nH_m in a general reaction of coke formation, δ_h be the molar hydrogen: feed stock ratio in the initial mixture, and $\Delta\nu$ be the change in the number of moles of the gases in the reaction ($\Delta\nu = \nu_{le} + \nu_h - 1$).

Hence (see Chap. 2), we have

$$\frac{K_p}{p^{\Delta\nu}} = K_x = \frac{(\nu_{le}y)^{\nu_{le}}(\delta_h + \nu_h y)^{\nu_h}}{(1-y)(1+\delta_h+\Delta\nu y)^{\Delta\nu}} \tag{6.27}$$

It follows from expression (6.27) that to lower the degree of conversion of the feed stock, i.e. to reduce the coke yield, it is not prudent to increase δ_h at a constant pressure because a change in δ_h alters the numerator and denominator of the expression of K_p approximately identically. If, on the other hand, the pressure in the system is produced by hydrogen, an increase in δ_h is attended by a simultaneous increase in the total pressure, and this results in a substantial decrease in y.

For example, for reaction 4 at 500 K, we have

$$K_p^\circ = \exp\left(\frac{29\,000}{8.31 \times 500}\right) = e^7$$

At a pressure in the system of 0.1 MPa and $\delta_h = 0$, we find that the degree of conversion of the feed stock $y = 0.9$ (or 90%). If, on the other hand, this reaction at a constant temperature is conducted at $\delta_h = 10$ and $p = 1$ MPa, we have $y = 0.01$, i.e. the reaction will involve only about 1% of the feed stock. This example shows the expediency of calculating the equilibrium yields of coke in the industrial processes where coke is the target or a side product.

6.3. Alkylation

Alkylation is carried out in the liquid or gas phases, and also in a mixed gas-liquid system. For simple and complex alkylation reactions, we usually succeed in obtaining analytical expressions relating the equilibrium constant and the product yields. These expressions are given below for homogeneous reactions, and it is assumed that the initial mixture contains no alkylation products.

1. *Simple reaction.* Let us assume that for an alkylation reaction of the form

$$A + B \rightarrow A_1 \tag{XVII}$$

y is the degree of conversion of A, m_0 and $m_{0,B}$ are the numbers of moles of A and B in the initial mixture, and $m_{0,B}/m_0 = \delta$. Hence,

$$K_x = \frac{x_{A_1}}{x_A x_B} = \frac{y(1+\delta-y)}{(1-y)(\delta-y)}$$

The positive solution of this quadratic equation has the form

$$y = \frac{(\delta+1) - \sqrt{(\delta+1)^2 - \frac{4K_x\delta}{K_x+1}}}{2}$$

Consequently, the calculations of the degree of conversion and the mole fractions of the components are not difficult to perform:

$$x_A = \frac{1-y}{1+\delta-y}, \quad x_B = \frac{\delta-y}{1+\delta-y}, \quad x_{A_1} = \frac{y}{1+\delta-y}$$

2a. *Parallel alkylation reaction.* Reactions will be parallel in which different alkyl derivatives of the same molecular mass form, for example, isomer alkanes with eight carbon atoms in the alkylation of butene with isobutane. The scheme of such a reaction is:

$$A + B \xrightarrow{K_{x_1}} A_1, \quad A + B \xrightarrow{K_{x_2}} A_2, \text{ etc.}$$

Let us designate the equilibrium fractions of A converted to A_1, A_2, . . . by y_1, y_2, ... Hence the numbers of moles of the components in an equilibrium mixture will be as follows:

$$m_A = m_0\left(1 - \sum y_i\right), \quad m_B = m_0\left(\delta - \sum y_i\right), \quad m_{A_1} = m_0 y_1$$
$$m_{A_2} = m_0 y_2, \ \ldots, \quad \sum m_i = m_0\left(1 + \delta - \sum y_i\right)$$

We obtain the following system of equations relating K_{x_i} and y_i:

$$K_{x_1} = \frac{y_1\left(1+\delta-\sum y_i\right)}{\left(1-\sum y_i\right)\left(\delta-\sum y_i\right)}$$

$$K_{x_2} = \frac{y_2\left(1+\delta-\sum y_i\right)}{\left(1-\sum y_i\right)\left(\delta-\sum y_i\right)}$$

. . . . . .

Therefore, $y_i = (K_{x_i}/K_{x_1})\, y_1$. Introducing the notation $\sum K_{x_i}/K_{x_1} = b$, we have $\sum y_i = by_1$. Hence

$$K_{x_1} = \frac{y_1(1+\delta-by_1)}{(1-by_1)(\delta-by_1)}$$

and

$$y_1 = \left[(\delta+1) - \sqrt{(\delta+1)^2 - \frac{4K_{x_1}b\delta}{K_{x_1}b+1}}\right] \Big/ 2b$$

Let us also express the mole fractions of the components in an equilibrium mixture in terms of y_1:

$$x_A = \frac{1-by_1}{1+\delta-by_1}, \quad x_B = \frac{\delta-by_1}{1+\delta-by_1}, \quad x_{A_i} = \frac{(K_{x_i}/K_{x_1})\,y_1}{1-\delta-by_1}$$

2b. Another type of a *parallel alkylation reaction* is the interaction of one reactant with isomers, for example, of isobutene (A) with various C_4 alkenes (B_i). Here the same product A_1 (isooctane) can form. The scheme of this reaction is as follows:

$$A + B_1 \xrightarrow{K_{x_1}} A_1, \quad A + B_2 \xrightarrow{K_{x_2}} A_1 \text{ etc.}$$

Let us designate, as previously, the equilibrium fractions of A converted to A_1 in each reaction by y_1, y_2, ... Hence the numbers of moles of the components in an equilibrium mixture will be as follows:

$$m_A = m_0\left(1-\sum y_i\right), \quad m_{B_1} = m_0(\delta_1 - y_1), \quad m_{B_2} = m_0(\delta_2 - y_2), \ \ldots,$$
$$m_{A_1} = m_0 - \sum y_i, \quad \sum m_i = m_0\left(1+\sum \delta_i - \sum y_i\right)$$

It has been taken into account here that there is no product A_1 in the initial mixture, and δ_i stands for the ratio of the numbers of moles of B_i and A in the initial mixture.

We obtain the following system of equations relating K_{x_i} and y_i:

$$K_{x_1} = \frac{\sum y_i\left(1+\sum \delta_i - \sum y_i\right)}{\left(1-\sum y_i\right)(\delta_1 - y_1)}$$

$$K_{x_2} = \frac{\sum y_i\left(1+\sum \delta_i - \sum y_i\right)}{\left(1-\sum y_i\right)(\delta_2 - y_2)}$$

. . . . . .

From this system, we find

$$y_i = \delta_i - \frac{K_{x_1}}{K_{x_i}}(\delta_1 - y_1), \quad \sum y_i = \sum \delta_i - \frac{\sum K_{x_i}}{K_{x_i}}(\delta_1 - y_1)$$

For brevity, we introduce the notation

$$\delta_1 - y_1 \equiv z, \quad \frac{\sum K_{x_i}}{K_{x_1}} \equiv 1/b, \ \sum \delta_i \equiv c$$

Therefore

$$K_{x_1} = \frac{(c-bz)(1+bz)}{(1+c+bz)\,z}$$

It is not difficult to find the solution of this quadratic equation, i.e. we can use the known values of K_{x_1} and δ_i to find y_1, and the lat-

ter to find y_i. Naturally, if one reaction proceeds, we have $\sum y_i \equiv \equiv y_1 \equiv y$, $\sum K_{x_i} \equiv K_{x_1} \equiv K_x$, and the equation relating K_{x_1} and y_1 will be the same as for a simple alkylation reaction.

3. *Consecutive alkylation reactions.* They include reactions that simultaneously yield alkyl derivatives having a various molecular mass, for example, mono-, di-, and trialkyl-substituted compounds:

$$A + B \xrightarrow{K_{x_1}} A_1, \quad A_1 + B \xrightarrow{K_{x_2}} A_2, \text{ etc.}$$

Here the notation A_i and K_{x_i} has a different meaning than in case 2. Let us assume, as previously, that $y_1, y_2, \ldots$ are fractions of A converted to $A_1, A_2, \ldots$. Hence the numbers of moles of the components in an equilibrium mixture are:

$$m_A = m_0(1 - \sum y_i), \quad m_B = m_0(\delta - \sum i y_i), \quad m_{A_i} = m_0 y_i$$
$$\sum m_i = m_0(1 + \delta - \sum i y_i)$$

It is not difficult to see that

$$y_i = \frac{K_{x_i}}{K_{x_1}} y_1, \quad \sum y_i = \frac{\sum K_{x_i}}{K_{x_1}} y_1 = b y_1$$
$$\sum i y_i = \frac{\sum i K_{x_i}}{K_{x_1}} y_1 = d y_1$$

where b and d are constants.

From the condition

$$K_{x_1} = \frac{y_1(1 + \delta - d y_1)}{(1 - b y_1)(\delta - d y_1)}$$

we find:

$$y_1 = \frac{(K_{x_1} b\delta + K_{x_1} d + \delta + 1) - \sqrt{(K_{x_1} b\delta + K_{x_1} d + \delta + 1)^2 - 4K_{x_1} d\delta (K_{x_1} b + 1)}}{2d(K_{x_1} b + 1)}$$

It is a simple matter to express the mole fractions of the components in an equilibrium mixture in terms of y_1:

$$x_A = \frac{1 - b y_1}{1 + \delta - d y_1}, \quad x_B = \frac{\delta - d y_1}{1 + \delta - d y_1}, \quad x_{A_i} = \frac{(K_{x_i}/K_{x_1}) y_1}{1 + \delta - d y_1}$$

Let us now consider the calculation of the equilibrium composition of a gas-liquid reaction conducted in an ideal solution:

$$A(lq) + B(g) \rightarrow A_1(lq)$$

We find the constant $K^{\circ}_{p,x}$ from the value of ΔG° determined according to the data of standard thermodynamic tables:

$$-\Delta G^{\circ} = RT \ln K^{\circ}_{p,x}; \quad K^{\circ}_{p,x} = \frac{x_{A_1(lq)}/x_{A(lq)}p_B}{x^{\circ}_{A_1(lq)}/x^{\circ}_{A(lq)}p^{\circ}}$$

A gas-liquid reaction is generally conducted under conditions when p_B is constant (the bubbling of a gas at atmospheric pressure or a constant pressure of the gas in an autoclave). Therefore from the known values of $K_{p,x}$ and p_B, we find

$$K_{x'} = K_{p,x}p_B = \frac{x_{A_1(lq)}}{x_{A(lq)}}, \quad K_{p,x} = K^{\circ}_{p,x}\frac{x^{\circ}_{A_1(lq)}}{x^{\circ}_{A(lq)}p^{\circ}} = \frac{K^{\circ}_{p,x}}{p^{\circ}}$$

It is quite obvious that the calculation of the composition of the liquid phase of a gas-liquid reaction according to the constants $K_{p,x}$ is similar to the calculation of equilibrium in isomerization (K'_x is the ratio of the mole fractions of the product and the reactant) considered above and does not involve any difficulties.

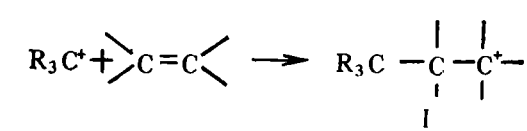
6.3.1. Alkylation of Alkanes with Alkenes

This reaction is thermodynamically possible at low temperatures and proceeds with the considerable evolution of heat. Consequently, elevation of the temperature is attended by the reverse reaction of cracking beginning to predominate. In the presence of acid catalysts (H_2SO_4, BF_3, $AlCl_3$, etc.), only iso-, but not *n*-alkanes, enter into the reaction; no normal alkanes are contained in the alkylate.

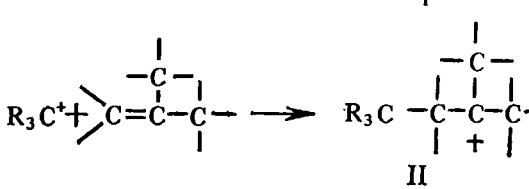
To establish the structure of the formed hydrocarbons, it is good to consider the carbocation mechanism of the relevant reaction. The reaction includes the attack of an isoalkane by a carbenium ion R^+ with the formation of a tertiary carbenium ion:

$$R^+ + R_3CH \rightarrow RH + R_3C^+ \qquad \text{(XVIII)}$$

Further, the tertiary carbenium ion is attached to an alkene molecule:

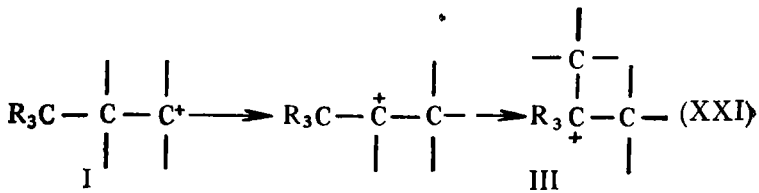


(XIX)



(XX)

Since the stability of the carbenium ions grows in the series: primary < secondary < tertiary, then isomerization of ion I is possible (but not of II):



The "heavy" tertiary carbenium ions II and III continue the chain according to reaction (XVIII) with an isoalkane.

For more high-molecular carbenium ions (with 10 or more carbon atoms), cracking is possible that results in the formation of a new alkene and alkane. This mechanism also indicates that if a catalyst and a solvent are used ensuring the stability of the secondary or even of the primary ion, the alkylation of alkenes by normal alkanes is also possible.

With a view to the considered mechanism, we have determined the main products of alkylation of isobutane by various alkenes, and also of propane and butane by ethylene. The heats and equilibrium constants of gas-phase alkylation with the formation of these products are presented in Table 66.

Examination of the data contained in Table 66 reveals that alkylation proceeds with the evolution of approximately 75-100 kJ per mole of alkylate, which is facilitated by low temperatures. It is also obvious ($K_x = K_p p$) that the degree of conversion grows with an increase in the pressure. The heats of the reactions depend only slightly on the temperature. At 300 K, and for many reactions also at 400 K, alkylation proceeds practically to the end at atmospheric and increased pressures. At higher temperatures, the thermodynamic restrictions become noticeable, so that at 800 K the conversion of the reagents will generally not exceed 2%, and in a number of cases—fractions of a per cent.

At relatively low temperatures, the alkylation of any alkane with any alkene is thermodynamically possible, so that difficulties encountered in the conducting of normal alkane alkylation reactions are due to kinetic factors. The same is indicated by the values of K_p for the reactions of alkylation of isobutane with various alkenes. The thermodynamic probability of a reaction decreases in the series ethylene > propylene > *n*-1-butene > 2-butene > isobutene, whereas as regards their reactivity the alkenes are arranged in the reverse sequence. It should be stressed in this connection that ethylene and the higher alkenes can be good alkylation agents from thermodynamic considerations.

Table 66. **Heats ΔH° (in kJ) and Equilibrium Constants K_p° for Alkylation**

Reaction	Tempera 300	
	$-\Delta H^\circ$	K_p°
Alkylation of Alkanes		
Ethylene + ethane → isobutane	102.2	5.3×10^8
Ethylene + propane → 2-methylbutane	103.0	2.0×10^9
Ethylene + *n*-butane → 3-methylpentane	97.8	6.6×10^7
Ethylene + isobutane → 2,3-dimethylbutane	95.6	7.7×10^8
Propene + isobutane → 2,3-dimethylpentane	85.1	1.3×10^7
n-Butene + isobutane → 2,2,4-trimethylpentane	89.50	21.7×10^5
1-Pentene + isobutane → 2,2,5-trimethylhexane	98.5	55.5×10^5
Isobutene + isobutane → 2,2,4-trimethylpentane	72.7	0.11×10^5
cis-2-Butene + isobutane → 2,2,4-trimethylpentane	82.6	2.4×10^5
trans-2-Butene + isobutane → 2,2,4-trimethylpentane	78.5	0.77×10^5
2-Methyl-2-butene + isobutane → 2,2,5-trimethylhexane	76.9	0.23×10^5
Alkylation of Aromatics		
Ethylene + benzene → ethylbenzene	105.4	$10^{11.7}$
Ethylene + ethylbenzene → 1,2-diethylbenzene	101.0	10^{10}
Ethylene + ethylbenzene → 1,3-diethylbenzene	103.9	10^{11}
Ethylene + ethylbenzene → 1,4-diethylbenzene	104.4	10^{11}
Ethylene + 1,2-diethylbenzene → 1,2,3-triethylbenzene	101.34	10^{10}
Ethylene + 1,2-diethylbenzene → 1,2,4-triethylbenzene	104.4	10^{11}
Ethylene + 1,3-diethylbenzene → 1,2,3-triethylbenzene	98.5	$10^{9.2}$
Ethylene + 1,3-diethylbenzene → 1,2,5-triethylbenzene	105.2	$10^{10.4}$
Propylene + benzene → *n*-propylbenzene	95.5	$10^{9.6}$
Propylene + benzene → isopropylbenzene	99.4	$10^{9.6}$
Benzene + *n*-1-pentene → pentylbenzene	96.4	$10^{9.7}$
Benzene + *n*-1-hexene → *n*-hexylbenzene	96.3	$10^{9.7}$
Naphthalene + ethylene → 1-ethylnaphthalene	106.6	10^{11}
Naphthalene + ethylene → 2-ethylnaphthalene	107.4	$10^{11.7}$
Alkylation of Cycloalkanes		
Ethylene + cyclohexane → ethylcyclohexane	100.0	$10^{10.5}$
Propylene + cyclohexane → propylcyclohexane	90.6	$10^{8.2}$
1-Butene + cyclohexane → *n*-butylcyclohexane	89.9	$10^{8.1}$
Ethylene + cyclopentane → ethylcyclopentane	102.1	$10^{10.8}$
Propylene + cyclopentane → propylcyclopentane	91.3	$10^{8.4}$
1-Butene + cyclopentane → *n*-butylcyclopentane	90.9	$10^{8.4}$

On the basis of the values of K_p° given in Table 66, it is not difficult to calculate the equilibrium degrees of conversion y, and from them the equilibrium compositions. Such calculations are given below for the reactions of producing a technically important raw material, namely, 2,2,4-trimethylpentane (isooctane).

Reactions in an Ideal Gas Mixture. Let us first consider the reaction of preparing isooctane from isobutene and isobutane (K_p° is the

Reactions in an Ideal Gas Mixture

ture, K							
400		500		600		800	
$-\Delta H°$	K_p°	$-\Delta H°$	K_p°	$-\Delta H°$	K_p°	$-\Delta H°$	K_p°
with Alkenes							
101.8	1.9×10^5	101.2	425.6	100.3	7.46	98.5	0.05
102.6	6.8×10^5	102.1	1435.5	101.3	24.4	99.5	0.16
97.5	8.9×10^4	96.9	257.0	96.4	5.3	94.9	0.04
95.4	5.4×10^4	95.02	175.8	94.5	3.9	93.0	0.04
84.6	2.6×10^4	83.85	16.8	83.05	0.6	81.2	0.01
88.8	282.5	88.16	1.4	87.4	0.04	85.6	52×10^{-5}
97.7	2.9×10^3	96.48	8.5	95.0	0.2	91.6	17×10^{-4}
72.3	7.6	71.84	0.10	71.2	0.006	69.5	17×10^{-5}
81.3	66.2	79.87	0.4	78.5	0.02	75.9	45×10^{-5}
77.9	30.3	77.15	0.3	76.2	0.01	74.2	30×10^{-5}
75.6	10.5	73.9	0.1	71.9	0.006	67.7	19×10^{-5}
with Alkenes							
105.0	$10^{7.1}$	104.5	10^4	103.9	337.3	102.4	1.91
100.0	$10^{5.6}$	99.0	1030	98.1	19.8	96.4	0.15
103.4	$10^{6.2}$	102.8	3499	102.1	57.7	100.6	0.36
103.9	10^6	103.5	2023	102.9	32.3	101.7	0.19
101.1	$10^{5.6}$	100.9	877.0	100.6	15.4	99.7	0.10
104.2	$10^{6.6}$	103.9	6871	103.6	107.9	102.5	0.61
97.7	10^5	97.2	258	96.7	5.3	95.5	0.04
104.8	$10^{5.9}$	104.4	1327	103.9	20.4	102.6	0.12
94.8	$10^{5.4}$	93.9	887	92.9	20.9	90.8	0.21
98.7	$10^{5.3}$	97.7	529.7	96.6	10.8	94.2	0.09
95.7	$10^{5.5}$	94.9	1026	94.0	23.3	92	0.22
95.6	$10^{5.5}$	94.7	1002	93.8	23.0	91.8	0.2
105.6	$10^{6.8}$	104.5	10^4	103.3	169.8	100.9	1.0
106.4	10^7	105.4	$10^{4.3}$	104.4	263.0	102.4	1.5
with Alkenes							
99.8	$10^{6.7}$	98.5	3548	97.2	70.2	94.6	0.5
89.0	$10^{4.3}$	87.2	89.3	85.3	2.82	81.9	0.04
88.2	$10^{4.2}$	86.5	79.1	84.7	2.56	81.3	0.04
101.2	$10^{6.4}$	100.3	5236	99.5	95.5	97.7	0.7
90.08	$10^{4.5}$	88.9	142.6	87.7	4.15	85.3	0.05
89.7	$10^{4.5}$	88.5	137.1	87.4	4.05	85.1	0.05

lowest). Below are given the equilibrium degrees of conversion of an alkene at various temperatures, pressures, and alkane:alkene ratios (Table 67).

It can be seen from the data in Table 67 that at 300 K the degree of conversion can reach 100%. At 400 K, an increased pressure and dilution are needed to achieve a conversion of 98%. At higher temperatures, the degree of conversion drops sharply, and already at

Table 67. **Equilibrium Degree of Conversion of Isobutene in the Reaction Isobutene + Isobutane → Isooctane Conducted in an Ideal Gas Mixture**

Temperature, K	K_p°	Pressure, MPa	Molar ratio alkane:alkene	y, fractions
300	0.11×10^5	0.1	1	≈ 1
			5	≈ 1
		1.0	1	≈ 1
			5	≈ 1
400	7.6	0.1	1	0.66
			5	0.86
		1.0	1	0.89
			5	0.98
500	0.1	0.1	1	0.05
			5	0.08
		1.0	1	0.30
			5	0.45
600	0.06	0.1	1	0.003
			5	0.005
		1.0	1	0.03
			5	0.05
800	17×10^{-5}	0.1	1	≈ 0
			5	≈ 0
		1.0	1	≈ 0
			5	≈ 0

600 K a reaction may involve not over 5% of a reactant. The degree of conversion is affected to a larger extent by the pressure than by the molar ratio of the reactants.

Different alkenes with four carbon atoms participate in alkylation in real processes of isooctane production. The equilibrium degrees of conversion of *n*-alkenes are somewhat higher than of isooctane, but in alkylation of mixtures of various alkenes with isobutane, the yield of the alkylate will not exceed that indicated in Table 67.

Thus, if a mixture of 25% of *n*-1-butene, 25% of *cis*-2-butene, 25% of *trans*-2-butene, and 25% of isobutene participates in alkylation, and the latter is conducted at 500 K, 0.1 MPa, and the ratio of the alkane to the alkenes is unity (that of the alkane to an individual alkene is four), then calculations by the expressions given at the beginning of this section yield the following system of equations:

$$1.4 = \frac{\sum y_i\,(2-\sum y_i)}{\left(\frac{1}{4} - y_1\right)\left(1-\sum y_i\right)}, \quad 0.3 = \frac{\sum y_i\,(2-\sum y_i)}{\left(\frac{1}{4} - y_2\right)\left(1-\sum y_i\right)}$$

$$0.4 = \frac{\sum y_i\,(2-\sum y_i)}{\left(\frac{1}{4} - y_3\right)\left(1-\sum y_i\right)}, \quad 0.1 = \frac{\sum y_i\,(2-\sum y_i)}{\left(\frac{1}{4} - y_4\right)\left(1-\sum y_i\right)}$$

Its solution is $\sum y_i \approx 0.03$, i.e. about 3% of the alkane enters into the reaction. This value is less than that given in Table 67 for a simple reaction because of the four-fold reduction of the initial concentration of each alkene isomer.

Reaction in an Ideal Solution. To calculate the equilibrium composition of an ideal solution, one can use data on the equilibrium ideal gas mixture. In accordance with the relations given in Chap. 2, we have

$$K_p = K_{x^{\mathrm{lq}}} K_p^\circ$$

where K_p and $K_{x^{\mathrm{lq}}}$ are the equilibrium constants of a reaction in the gas and liquid phases, respectively, and K_p° is a function of the saturated vapour pressure of the components at the temperature of the reaction.

For isobutene, isobutane, and isooctane at 300 K, we have $p_A^\circ = 0.32$, $p_B^\circ = 0.37$, and $p_{A_1}^\circ = 0.005$ MPa, respectively:

$$K_p^\circ = \frac{0.005}{0.32 \times 0.37} = 0.042 \text{ MPa}^{-1}$$

Since for this temperature $K_p = K_p^\circ/0.1 = 1.1 \times 10^5$ MPa^{-1} (see Table 66), we have

$$K_{x^{\mathrm{lq}}} = \frac{1.1 \times 10^5}{0.042} = 26.2 \times 10^5$$

For 400 K, we have $p_A^\circ = 2.94$, $p_B^\circ = 3.16$, $p_{A_1}^\circ = 0.16$ MPa, $K_p^\circ = 0.017$, $K_p = 76$ MPa^{-1}, and, consequently, $K_{x^{\mathrm{lq}}} = 4.5 \times 10^3$.

The values of $K_{x^{\mathrm{lq}}}$ are larger than K_p by one or two orders of magnitude. This signifies that the conducting of a reaction in the liquid phase enables one to obtain higher degrees of conversion in comparison with a gas-phase reaction at moderate pressures. This is one of the reasons why under industrial conditions the alkylation of C_3 and C_4 alkenes with isobutane is conducted in the liquid phase at temperatures of 0-10 °C (the catalyst is H_2SO_4) or of 30-40 °C (the catalyst is HF).

The use of solid acid catalysts requires higher temperatures (up to 300 °C), and also higher pressures (1-20 MPa) to ensure favourable thermodynamic conditions.

It should be noted that the formation of C_{12} hydrocarbons from a C_4 alkene and isooctane at moderate temperatures is quite probable thermodynamically, i.e. the reaction of alkylation of the alkane with the alkene can proceed as a consecutive one, but in real processes the formation of polyalkyl-derivatives is not great because of kinetic hindrances.

6.3.2. Alkylation of Aromatics with Alkenes

This reaction, owing to its exothermic nature, is also promoted by low temperatures, but its thermodynamic probability is substantial at high temperatures (800 K). For example, if the minimum value of the equilibrium constant for the alkylation of alkanes with alkenes at 800 K is 17×10^{-5}, then for the alkylation of aromatic hydrocarbons with alkenes it is 0.04 (see Table 56). At 300-600 K, alkylation can be performed with virtually complete using up of one of the reactants.

The evolution of heat in the alkylation of aromatics with alkenes is somewhat higher than in the alkylation of alkanes.

The heats and equilibrium constants are close in the alkylation of benzene with alkenes of a various molecular mass.

In the alkylation of naphthalene, the evolution of heat and the equilibrium constants are somewhat higher than in the alkylation of benzene, the attachment of an alkyl group in the 1 and 2 positions occurring with close thermodynamic characteristics.

It is interesting that alkylation with the formation of either *n*-alkylbenzenes or *sec*-alkylbenzenes is equally probable thermodynamically, whereas *sec*-alkylbenzenes are mainly obtained in an experiment with C_3 and higher alkenes. This is explained by the intermediate formation of *sec*-carbenium ions, and their attachment to the benzene ring occurs with the formation of a sigma complex; if the nucleus contains a hydrocarbon substituent, an *ortho*- or *para*-dialkyl-substituted compound forms (see p. 261).

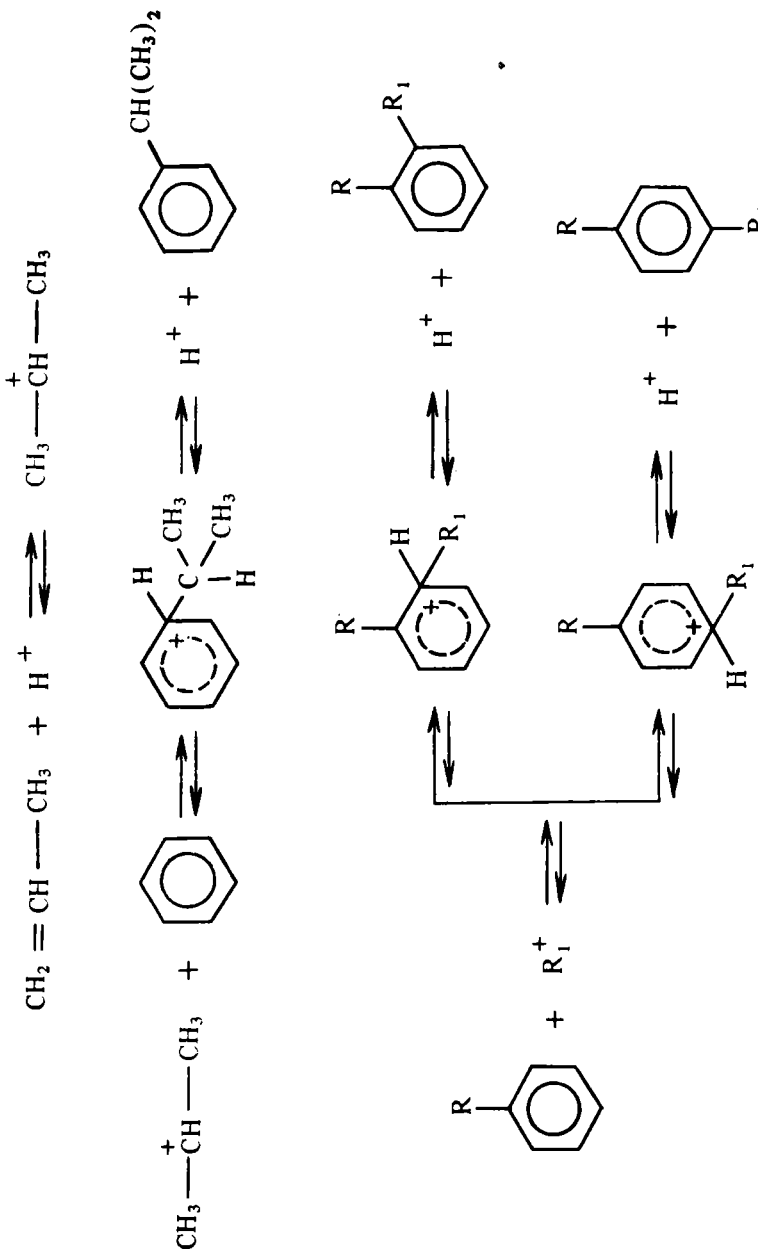
The thermodynamic probability of the reaction of aromatics with alkenes decreases insignificantly when going over from ethylene to propylene, but remains approximately constant with a further growth in the number of carbon atoms in the alkene.

From the values of K_p° given in Table 66, it is not difficult to calculate the equilibrium degrees of conversion y using the expressions given above that relate y and K_x, where $K_x = K_p^\circ p/p^\circ$ (p° is the standard pressure).

For a simple alkylation reaction, the equilibrium degrees of conversion will be as follows:

K_x	0.1	0.5	1	2	5	10	20	50	100	1000
y at $\delta = 1$	0.045	0.085	0.30	0.42	0.59	0.70	0.78	0.85	0.90	0.97
y at $\delta = 5$	0.075	0.29	0.45	0.62	0.80	0.89	0.94	0.98	0.99	1.00

At a pressure of 0.1 MPa (the standard value), alkylation is possible practically to the end at temperatures up to 500 K, especially if increased pressures or dilution are used. At 600 K, the degree of conversion can range from 60 to 100% (depending on the nature of the reactants, the pressure, and dilution), and at 800 K, from 3 to 40%. Consequently, when studying alkylation at temperatures


CH(CH3)2
CH2 = CH — CH3 + H+
CH3 — CH — CH3
H+ +
H
C
CH3
CH3
H
R
R1
R1
R
H
R1
R
R1
H
R
R1
+
H+
R1+
R

up to 500 K, we give our main attention to the distribution of the products of a parallel or consecutive reaction [43], but it is the same as in the isomerization (see above) of alkylbenzenes.

The conducting of an alkylation reaction in a real gas phase at moderate temperatures (up to 500 K) does not affect substantially the equilibrium degree of conversion. For the alkylation of aromatics with alkenes at 300 K, the constant K_{γ° is about 0.97 at 0.1 MPa and about 0.7 at 5 MPa; at 400 K it is 0.99 and 0.8, respectively. At these values, the constant K_p in a real gas mixture has an order of magnitude of 10^3, i.e. the equilibrium degree of conversion will be close to 100%.

The conducting of a reaction in the liquid phase, as in the alkylation of alkanes with alkenes, is more favourable thermodynamically than in the gas phase, but this is not significant. In both cases, a degree of conversion exceeding 99% is possible.

Alkylation is often conducted in a gas-liquid system with the use of a gaseous alkene. The calculations for this case have been considered on an earlier page. Below we compare the values of ΔG°, ΔH°, and K_p° for the alkylation of benzene with ethylene in the gas and gas-liquid phases at 300 K:

Reaction	ΔH°_{300}, kJ	ΔG°_{300}, kJ	K_p° ($K^\circ_{p,x}$)
$C_6H_6(g) + C_2H_4(g) \rightarrow C_6H_5{-}C_2H_5(g)$	−105.4	−64.4	25.8
$C_6H_6(lq) + C_2H_4(g) \rightarrow C_6H_5{-}C_2H_5(lq)$	−113.8	−74.9	30.1

The reaction in the gas-liquid system is obviously more probable thermodynamically. At moderate temperatures, alkylation in a gas-liquid system is possible up to the virtually complete consumption of one of the reactants. At elevated temperatures (and, accordingly, elevated pressures), K_p° will decrease, but even at 500 K the reaction proceeds practically to the end.

6.3.3. Alkylation of Cycloalkanes with Alkenes

This reaction is thermodynamically possible within a broad range of temperatures—even at 800 K the equilibrium constants differ noticeably from zero. Lowering of the temperature is naturally attended by an increase in the equilibrium constants because the heat of this exothermic reaction (from −85 to −100 kJ/mol) is appreciable.

It can be seen from the data in Table 66 that the thermodynamic characteristics of alkylation of both cyclohexane and cyclopentane are close. Since already at 600 K the degree of conversion can be less than 100%, the constants K_{γ° have been estimated, which take into account the non-ideal nature of the system.

In the range of temperatures of 400-800 K and pressures of 0.1-5 MPa, the value of K_{γ° differs insignificantly from unity (from 0.92

to 1). Consequently, the values of K_p° given in Table 66 can be used to estimate the equilibrium composition at elevated pressures.

In concluding, let us compare the equilibrium degrees of conversion in the alkylation of isobutane, benzene, and cyclohexane with ethylene in an ideal gas phase at standard pressure (see Table 68).

Table 68. **Comparison of the Alkylation of Selected Hydrocarbons with Ethylene in an Ideal Gas Phase at Standard Pressure and a Molar Ratio of the Reactants Equal to Unity**

Reaction	Equilibrium degree of conversion y (fractions) at temperature, K		
	300	500	800
Ethylene + isobutane → 2,3-dimethylbutane	1	0.95	0.02
Ethylene + benzene → ethylbenzene	1	0.99	0.41
Ethylene + cyclohexane → ethylcyclohexane	1	0.98	0.18

A glance at Table 68 reveals that the temperature has the greatest effect on the alkylation of alkanes with alkenes.

6.4. Polymerization and Polycondensation

In analysing low-molecular polymerization, below we use the classical approach because there are no difficulties in determining the thermodynamic functions of the feed stock and products. The processes of producing high-molecular compounds have a number of features and are treated separately. Generally the thermodynamic functions of the products cannot be determined for them, therefore the probability of representative reactions of the initiation and growth of the polymer chain is studied. In this connection, the thermodynamic and kinetic analyses are combined. In the production of high-molecular compounds, one must take into consideration the heterogeneous nature of the reactions; here the product can be partly crystalline and be characterized only by the mean degree of polymerization (sometimes by the law of polymer distribution by molecular mass).

The thermodynamic analysis of the processes of low- and high-molecular polymerization made it possible to explain a number of experimental data. For example, 1-methylstyrene polymerizes at atmospheric pressure at temperatures below 65 °C; conversely, sulphur forms interesting polymer molecules with opening of the ring at temperatures above 180 °C. The explanation of this was found by studying how the quantity ΔG is affected at various temperatures by the heat and the change in the entropy in polymerization, and

also by using notions of the upper and lower extreme temperatures of polymerization (see below). It became clear why a polymer of acetone cannot be obtained (owing to the low extreme temperature of polymerization), although polymers of other carbonyl compounds have been synthesized, and so on.

The investigations in the field of high-molecular polymerization have been summarized by Sawada [44], but the thermodynamic analysis requires further development because the accuracy of predicting ΔH, ΔS, and ΔG is meanwhile not high enough. This is why we consider below only the most representative data and effective working relations.

6.4.1. Gas-Phase Oligomerization of Alkenes

The first thermodynamic calculations [34, 45, 46] were devoted to determining the thermodynamic probability of carrying out the dimerization of alkenes at various temperatures. It was established that at temperatures up to about 500 K, the equilibrium constants of alkene dimerization with the obtaining of a 1-dimer are quite large, but at higher temperatures they rapidly decrease. With a growth in the molecular mass of the monomer, these constants decrease when going over from ethylene to 1-pentene, and then remain constant. Figure 23 shows how the value of ΔG° for polymerization changes with the temperature, while Tables 69 and 70 present ΔG° and the equilibrium constants of dimerization of 1-alkenes to 1-alkenes depending on the temperature.

Although in the calculations indicated above several obsolete values of the thermodynamic functions were used, the order of magnitude of the functions is correct. In this connection, we shall estimate the degrees of conversion of a monomer for various rate constants and pressures in the system. For the equilibrium constant K_p and the degree of conversion y as applied to dimerization reactions, we have $K_p^\circ = K_p p^\circ = K_x p^\circ / p$

$$K_p^\circ = \frac{\frac{1}{2} y \left(1 - \frac{1}{2} y\right)}{(1-y)^2} \frac{p^\circ}{p}$$

whence

$$y = \frac{(4K_p^\circ p/p^\circ) + 1 - \sqrt{(4K_p^\circ p/p^\circ) + 1}}{(4K_p^\circ p/p^\circ) + 1}$$

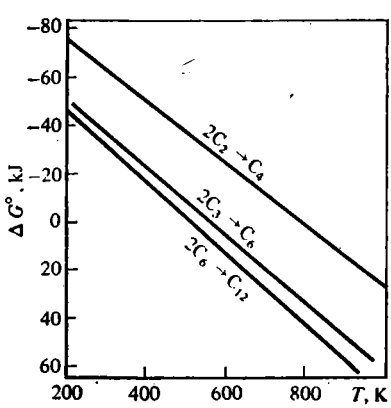


Fig. 23. Standard change in the Gibbs energy in the gas-phase dimerization of l-alkenes to l-alkenes

Table 69. **Standard Gibbs Energy of Dimerization of 1-Alkenes to 1-Alkenes**

Monomer	Dimer	ΔG° (in kJ) at temperatures, K		
		300	600	900
Ethylene	1-Butene	−64.2	−25.0	12.8
Propylene	1-Hexene	−38.4	5.0	45.6
1-Butene	1-Octene	−39.7	5.0	48.1
1-Pentene	1-Decene	−36.0	10.5	54.8
1-Decene	1-Eicosene	−36.0	12.0	54.8

Table 70. **Equilibrium Constants of Dimerization of 1-Alkenes to 1-Alkenes**

Monomer	Dimer	K_p° at temperatures, K					
		300	400	500	600	800	1000
Ethylene	1-Butene	1.6×10^{11}	4.3×10^6	8.1×10^3	1.5×10^2	0.95	5×10^{-2}
Propylene	1-Hexene	3.4×10^6	9.6×10^2	6.3	0.3	5.4×10^{-3}	5.6×10^{-4}
1-Butene	1-Octene	2.9×10^6	10×10^2	10	0.3	5.8×10^{-3}	5.3×10^{-4}
1-Pentene	1-Decene	2.0×10^6	4.6×10^2	3	0.1	2.4×10^{-3}	2.3×10^{-4}
1-Alkene (C_6 and higher)		2.0×10^6	4.0×10^2	3	0.1	2.4×10^{-3}	2.3×10^{-4}

The solution holds for values of $(4K_p^\circ p/p^\circ) + 1$ exceeding unity. To illustrate the relation between the quantities $K_p^\circ p/p^\circ$ and y for the dimerization of alkenes, we shall present some results of calculations by the equation obtained:

$(4K_p^\circ p/p^\circ) + 1$ . . .	1000	100	40	30	20	10	5	2	1.5	1.1
y	0.97	0.90	0.84	0.82	0.78	0.68	0.45	0.30	0.19	0.05

It is obvious that at values of the quantity $K_p^\circ p/p^\circ$ exceeding 250, the degree of conversion of the monomer will exceed 95%, whereas at values of this quantity below 0.025, the degree of conversion will not exceed 5%. Consequently, it is prudent to determine the equilibrium degrees of conversion if the quantity $K_p^\circ p/p^\circ$ is within 0.025 to 250.

Prior to discussing the possible degrees of conversion in the dimerization of alkenes, let us compare the equilibrium constants for the processes of formation of normal 1-alkenes, normal 2-alkenes, and isoalkenes (Table 71), because in real processes dimers with a various structure form.

Table 71. **Equilibrium Constants for the Dimerization of Ethylene and Propylene with the Formation of Dimers with a Various Structure**

Monomer	Dimer	K_p° at temperatures, K		
		300	500	700
Ethylene	1-Butene	1.6×10^{11}	8.1×10^{3}	6.6
	cis-2-Butene	1.6×10^{12}	2.5×10^{4}	10.0
	Isobutene	3.2×10^{13}	1.3×10^{5}	31.6
Propylene	1-Hexene	3.4×10^{6}	6.3	0.1
	cis-2-Hexene	6.3×10^{6}	39.8	0.1
	2-Methyl-1-pentene	1.3×10^{9}	199.5	0.3

It follows from the data in the table that the formation of dimers of a various structure is thermodynamically probable; here for different monomers the formation of alkenes with a double inner bond is more probable thermodynamically than the formation of 1-alkenes, while the probability of the formation of alkenes with a branched structure is still higher. This does not naturally signify that in real dimerization processes isoalkenes form first of all, then alkenes with an inner double bond, and only last of all 1-alkenes. The proper choice of the catalyst and of the conditions of dimerization enables one to create kinetic hindrances for the formation of certain types of dimers and conduct dimerization selectively, for example with the obtaining of only 1-alkenes or only isoalkenes.

Naturally, in many dimerization processes, a mixture of dimers varying in structure forms. Thus, ethylene in the presence of a catalyst—a cobalt salt on active carbon—has yielded *n*-butenes with a predominating content of 2-butenes at low and 1-butenes at high rates of supplying the feed stock [34]. Here the formation of dimers differing in their structure is determined not by thermodynamic, but by kinetic factors, and this is typical of most technical processes.

One must bear in mind, however, that if dimerization is conducted at a relatively high temperature so that the value of $K_p^\circ p$ does not exceed two, the thermodynamic restrictions preventing the formation of dimers become especially appreciable, and in this case the main product of dimerization will be the one for which the value of $K_p^\circ p$ is higher. In this connection, when comparing thermodynamic calculations and experimental equilibrium conversions and compositions, one must take into account whether only one dimer or dimers of a various structure form. In the latter case with a limited degree of conversion for the formation of one dimer, the overall degree of conversion of the monomer will be higher because of the proceeding of

several parallel reactions. We shall show how the composition is calculated for complex dimerization with the formation of several types of dimer molecules.

Assume that in the dimerization of monomer M different dimer molecules D_1, D_2, . . ., D_k form simultaneously, so that the chemical scheme of the process is

$$2M \rightarrow D_1, \quad 2M \rightarrow D_2, \ \ldots, \ 2M \rightarrow D_k$$

For the equilibrium constants of each of the k parallel steps, we find

$$K_{p_1} = \frac{p_{D_1}}{p_M^2}, \quad K_{p_2} = \frac{p_{D_2}}{p_M^2}, \ \ldots, \ K_{p_k} = \frac{p_{D_k}}{p_M^2}$$

If the overall degree of conversion of the monomer in all the steps is y, while the degree of conversion in the i-th step is y_i and $y = \sum y_i$, then for the number of moles of the components m_M, m_i, and the sum of the moles in the equilibrium system $\sum m_i$, we have

$$m_M = m_{0M}(1-y); \quad m_{D_1} = \frac{1}{2} m_{0M} y_1, \ \ldots, \ m_{D_k} = \frac{1}{2} m_{0M} y_k$$

$$\sum m_i = m_{0M}\left(1 - \frac{1}{2} y\right)$$

If we now express the equilibrium constants in terms of the overall degree of conversion y and the degrees of conversion for the separate steps y_1, . . ., y_k, we have

$$K_{p_1} = \frac{\frac{1}{2} y_1 \left(1 - \frac{1}{2} y\right)}{(1-y)^2} \frac{1}{p}, \quad K_{p_2} = \frac{\frac{1}{2} y_2 \left(1 - \frac{1}{2} y\right)}{(1-y)^2} \frac{1}{p}, \ \ldots,$$

$$K_{p_k} = \frac{\frac{1}{2} y_k \left(1 - \frac{1}{2} y\right)}{(1-y)^2} \frac{1}{p}$$

The sum of these equations yields an equation for determining y that is similar to the one obtained earlier for one reaction:

$$y = \frac{4p\left(\sum_i K_{p_i}\right) + 1 - \sqrt{4p\left(\sum_i K_{p_i}\right) + 1}}{4p\left(\sum_i K_{p_i}\right) + 1}$$

The solution of this equation is the same as above, but instead of K_p°/p° we must introduce $\sum_i K_{p_i}$. We find the degree of conversion of the feed stock in the i-th direction from the conditions

$$y_i = \frac{K_{p_i}}{\sum_i K_{p_i}} y, \quad \sum_i y_i = y$$

There is sense in calculating the degrees of conversion for complex equilibria only if for all the steps the degrees of conversion (or the product $K_{p_i}p$) are both not very high and not very low. In accordance with the above analysis, we can recommend the conducting of such calculations if $\sum_i K_{p_i}p$ is within the interval from 0.025 to 250. Below we compare the equilibrium degrees of conversion of monomers (ethylene and propylene) in simple and complex dimerizations at various temperatures (Table 72).

Table 72. **Equilibrium Degrees of Conversion of Ethylene and Propylene in Dimerization**

Monomer	Dimer	Degree of conversion at temperatures (in K) and pressures (in MPa)					
		300		500		700	
		0.1	5	0.1	5	0.1	5
Ethylene	1-Butene	>0.99	>0.99	>0.99	>0.99	>0.81	>0.97
	2-Butene	>0.99	>0.99	>0.99	>0.99	>0.84	>0.98
	Isobutene	>0.99	>0.99	>0.99	>0.99	>0.91	>0.99
	All three dimers	>0.99	>0.99	>0.99	>0.99	>0.93	>0.99
Propylene	1-Hexene	>0.99	>0.99	0.81	0.97	0.16	0.78
	cis-2-Hexene	>0.99	>0.99	0.92	0.99	0.16	0.78
	2-Methyl-1-pentene	>0.99	>0.99	0.96	0.99	0.33	0.88
	All three dimers	>0.99	>0.99	0.97	>0.99	0.42	0.90

A close look at the data in Table 72 reveals that when the possibility of the formation of several dimer molecules is taken into account, appreciable changes are introduced into the calculations of the equilibrium degree of conversion at low conversions. Thus, if the dimerization of ethylene into 1-butene at 700 K and 0.1 MPa is possible with the conversion of 81% of the monomer, then when the possibility of the formation of three different dimers is taken into consideration, this value grows only to 93% (by 13% relative to the former value). At the same time, the dimerization of propylene under the same conditions to 1-hexene is possible with conversion of the feed stock by 16%, and to all three isomers, by 42% (a growth of 2.6 times).

With an increase in the molecular mass of the monomer, as already noted, the equilibrium constants of dimerization decrease to a certain value that becomes constant for alkenes with five and more carbon atoms. The equilibrium of dimerization of the higher alkenes is calculated according to the relations given above. Since, however, for such alkenes the number of possible dimer structures formed grows sharply, illustrative model calculations carry little informa-

tion. It is prudent to perform the calculations for specific dimerization conditions with account taken of the structures of the formed dimers because, as for propylene, depending on the number of dimers formed the degree of conversion can change several times.

We must not fail to note the strong effect of the pressure on the equilibrium degree of conversion. The conducting of the process at high pressures makes it possible to increase the degree of conversion and bring it up to 90%.

Dimerization reactions proceed with an appreciable liberation of heat; for monomers with four or more carbon atoms, the heat of a reaction depends only slightly on the molecular mass of the feed stock, as can be seen from the data in Table 73. It is also clear that

Table 73. **Heats of Dimerization of Lower Alkenes**

Monomer	Dimer	Heat $-\Delta H°$ of producing 1 mol of a dimer (in kJ) at temperatures, K		
		300	500	700
Ethylene	1-Butene	96.5	104.2	103.4
Propylene	1-Hexene	78.7	81.2	79.1
1-Butene	1-Octene	82.8	81.2	79.5
1-Pentene	1-Decene	82.4	81.2	79.1

the heat of dimerization depends only slightly on the temperature: changes in $\Delta H°$ of 2-4 kJ with a change in the temperature of 400 K cannot be considered as substantial. The structure of the formed dimer is significant in the heat calculations of dimerization. To confirm this, let us consider the heats of dimerization of ethylene and propylene with the obtaining of dimers varying in structure (Table 74).

Table 74. **Heats of Dimerization of Ethylene and Propylene**

Monomer	Dimer	Heat $-\Delta H°$ of producing 1 mol of a dimer (in kJ) at temperatures, K		
		300	500	700
Ethylene	1-Butene	96.5	104.2	103.4
	cis-2-Butene	103.3	112.5	112.8
	Isobutene	113.4	120.5	119.6
Propylene	1-Hexene	78.7	81.2	79.1
	cis-2-Hexene	89.5	88.7	87.4
	2-Methyl-1-pentene	97.9	95.4	92.9

The evolution of heat is the smallest in the production of a 1-alkene, and the greatest in the production of a skeleton isoalkene. The differences in the evolution of heat in the production of dimers varying in structure from the same monomer reach 20 kJ per mole of dimer formed, which is 20-25% of the heat of the reaction.

Let us now consider the thermodynamic characteristics of oligomerization, when trimers, tetramers, and so on are the products. It follows from the relevant calculations [34, 46] that the change in the quantity ΔG° when a monomer unit is attached is constant if the unit is attached to a dimer, trimer, and so on (but not to a monomer). At 300 K, it is —38.5 kJ, at 600 K it is 6.3 kJ, and at 900 K it is 48.0 kJ for various monomers. When discussing this, Jessup [45] showed that if the heat and entropy components in the change in the Gibbs energy when a monomer unit is added are constant, then for a high-molecular polymer the change in ΔG° per mole of monomer doubles in comparison with similar changes in the formation of a dimer. That the calculated data are consistent with this statement can be seen from Table 75.

Table 75. **Values of ΔG° and ΔH° in Oligomerization**

Number n of monomer units in polymer	$-\frac{\Delta G^\circ}{n}$, kJ	Ratio $\left(+\frac{\Delta G^\circ}{n}\right)_n \Big/ \left(\frac{\Delta G^\circ}{n}\right)_{n=2}$	$-\frac{\Delta H^\circ}{n}$, kJ	Ratio $\left(+\frac{\Delta H^\circ}{n}\right)_n \Big/ \left(\frac{\Delta H^\circ}{n}\right)_{n=2}$	Theoretical ratio
2	19.2	1	41.2	1	—
3	25.1	1.31	54.9	1.33	1.33
4	28.1	1.46	61.8	1.5	1.5
5	29.9	1.56	65.9	1.6	1.6
6	31.1	1.62	68.6	1.66	1.66
	—	—	—	—	2

Calculations for the heat of a reaction agree better with the conception considered above than for the change in the Gibbs energy. This is associated with the fact that the changes in the entropy are not so constant as the changes in the heats when monomer units are attached. But for sufficiently good estimates of the thermodynamic characteristics of gas-phase polymerization, we can use the expressions

$$\Delta G_n^\circ = \Delta G_2^\circ + C_1 (n-2)$$
$$\Delta H_n^\circ = \Delta H_2^\circ + C_2 (n-2)$$

where ΔG_n° and ΔH_n° are the Gibbs energy and enthalpy of polymerization with the formation of a polymer from n monomer molecules, respectively, ΔG_2° and ΔH_2° are the same for the formation of a dimer, and C_1 and C_2 are constants.

Interesting results were obtained by calculations of the change in the Gibbs energy for the polymerization of propylene with the formation of polymers from dimers to pentamers (Fig. 24). The values of ΔG° change linearly with the temperature and pass through a single point corresponding to the zero value of ΔG° and a temperature between 500 and 600 K. In the region to the left of this point, the formation of more highly molecular polymers is thermodynamically more probable; in the region to the right, the formation of low-molecular ones is more probable, but this region is of no interest for the polymerization of propylene because of the low yields of the products. Thus, thermodynamic analysis shows that at low temperatures the formation of high-molecular polymers is more probable, while at high temperatures initially dimers will predominate, while with further elevation of the temperature the opposite process—depolymerization—will become the main one.

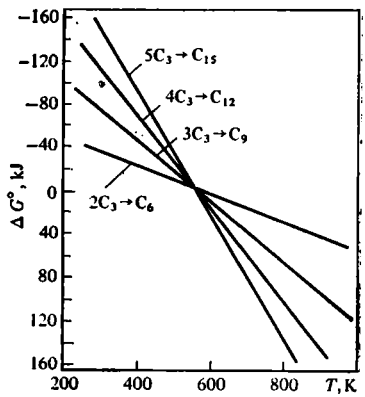


Fig. 24. Standard change in the Gibbs energy in the gas-phase oligomerization of propylene. High-molecular polymers are mainly formed in the region to the left of the point of intersection, and low-molecular ones—to the right of it

It will now be interesting to establish the composition of an equilibrium mixture of the products of multiple-step polymerization, i.e. the content of dimers, trimers, tetramers, and so on in an equilibrium mixture. It should be noted that such calculations have no meaning if the dimerization equilibrium constant is significant or the product $K_p p$ for dimerization has an order of magnitude of 100-250. For such a situation, the equilibrium constant of trimer formation is higher than that for a dimer, of a tetramer is higher than that for a trimer, and so on. Consequently, from thermodynamic considerations, we should expect the formation of practically only a polymer of the highest molecular mass from a monomer in an equilibrium mixture. Calculations for small values of $K_p p$ for dimerization also have no meaning because the degree of polymerization will be low, and the formation of polymers will be insignificant.

At limited values of $K_p p$ (from about 0.5 to about 250), thermodynamic calculations can be expedient for dimerization and the formation of various polymers in an experimental reactor. In a general case, having in view the possibility of the formation of polymers

varying in structure, the general methods of calculating the equilibrium composition of complex reactions (see Chap. 3) should be employed with the use of computers. But if a dimer, trimer, etc. can be considered as an individual substance, i.e. if polymerization can be described by the scheme

$$A_1 + A_1 \xrightarrow{K_{x_2}} A_2, \quad A_2 + A_1 \xrightarrow{K_{x_3}} A_3 \ldots A_{n-1} + A_1 \xrightarrow{K_{x_n}} A_n$$

then the known equilibrium constants K_{x_2}, $K_{x_3}, \ldots, K_{x_n}$ of the steps can be used to calculate the equilibrium composition as indicated below. The following expressions hold:

$$K_{x_2} = \frac{x_{A_2}}{x_{A_1}^2}, \quad x_{A_2} = K_{x_2} x_{A_1}^2$$

$$K_{x_3} = \frac{x_{A_3}}{x_{A_1} x_{A_2}}, \quad x_{A_3} = K_{x_3} x_{A_1} x_{A_2} = K_{x_3} K_{x_2} x_{A_1}^3$$

. . . . . .

or

$$K_{x_n} = \frac{x_{A_n}}{x_{A_1} x_{A_{n-1}}}, \quad x_{A_n} = K_{x_n} x_{A_1} x_{A_{n-1}} = K_{x_n} \ldots K_{x_3} K_{x_2} x_{A_1}^n \qquad (6.28)$$

Since the sum of the mole fractions of all the components equals unity, to calculate the unknown mole fraction of a monomer in an equilibrium mixture from the known equilibrium constants of the polymerization steps, we obtain the equation

$$x_{A_1} + K_{x_2} x_{A_1}^2 + \ldots + K_{x_n} \ldots K_{x_3} K_{x_2} x_{A_1}^n = 1 \qquad (6.29a)$$

We can modify this equation if we take into account that the product of the equilibrium constants of consecutive steps of polymerization gives the equilibrium constant of formation of the polymer from the monomer in one step:

$$K_{x_3} K_{x_2} = \frac{x_{A_3}}{x_{A_1} x_{A_2}} \frac{x_{A_2}}{x_{A_1}^2} = \frac{x_{A_3}}{x_{A_1}^3} = K_{x_{1\to 3}} \ldots K_{x_n} \ldots K_{x_3} K_{x_2} = K_{x_{1\to n}}$$

Here $K_{x_{1\to n}}$ is the equilibrium constant of the reaction $nA_1 \to A_n$. It can easily be calculated using the data of standard thermodynamic tables. We thus find:

$$x_{A_1} + K_{x_{1\to 2}} x_{A_1}^2 + \ldots + K_{x_{1\to n}} x_{A_1}^n = 1 \qquad (6.29b)$$

We find the mole fractions of the dimer, trimer, etc. in the equilibrium mixture from the value of x_{A_1} calculated by Eq. (6.29a) or (6.29b) and the known equilibrium constants:

$$x_{A_2} = K_{x_{1\to 2}} x_{A_1}^2, \ \ldots, \ x_{A_n} = K_{x_{1\to n}} x_{A_1}^n \qquad (6.30)$$

To find the root of the non-linear equation (6.29a) or (6.29b), it is prudent to use a search procedure such as the golden section (harmonic division) method [8]. It should be noted that although an equation of degree n enables us to obtain n roots, i.e. n values of x_{A_1} converting this equation into an identity, only one solution has a physical meaning (x_{A_1} can be within the interval from 0 to 1).

Let us illustrate the application of the above expressions for evaluating the equilibrium amounts of the dimer, trimer, and tetramer in the polymerization of ethylene to 1-alkenes at temperatures of 700 and 800 K. The equilibrium constants K_x when polymerization is conducted at a pressure of 0.1 MPa are as follows:

Reaction	Dimerization	Trimerization	Tetramerization
K_x at temperature:			
700 K	6.6	4.5	1.6
800 K	0.6	0.06	0.04

That the equilibrium constants decrease with a growth in the molecular mass of the polymer signifies that the calculations are being conducted for the "right-hand" region (see Fig. 24). By Eq. (6.29), we have:

for 700 K

$$x_e + 6.6x_e^2 + 4.5x_e^3 + 1.6_e^4 = 1$$

for 800 K

$$x_e + 0.6x_e^2 + 0.06x_e^3 + 0.04x_e^4 = 1$$

where x_e is the mole fraction of the monomer (ethylene) in an equilibrium mixture.

The roots of the obtained equations have been found to be $x_e \approx 0.29$ for 700 K and $x_e = 0.69$ for 800 K. In accordance with the relations given above, we shall further find the contents of the oligomers. For example, the content of the trimer in the equilibrium mixture at 700 K is $x_{A_3} = 4.5 \times 0.29^3 = 0.11$. We obtain the following results:

Oligomer	Monomer	Dimer	Trimer	Tetramer
Content of components in reaction mixture, mole fractions:				
at 700 K	0.29	0.59	0.11	0.01
at 800 K	0.69	0.28	0.02	0.01

These calculations show that by properly choosing the temperature, we can ensure conditions for obtaining only the dimer for the "right-hand" region. In practical studies, however, kinetic factors are used for this purpose.

The composition of the equilibrium mixture in the right-hand region is also greatly affected by the pressure. Its increase results both in a growth in the overall degree of conversion, which has been shown above, and in an increase in the fraction of the high-molecular polymer in the mixture. The explanation is that although the constants K_p do not depend on the pressure, the constants K_x employed in the calculations of the equilibrium compositions [Eqs. (6.29a) or (6.29b)] depend on the pressure. For the reaction $nA_1 \rightarrow A_n$, the constant $K_x = K_p p^{n-1} = Cp^{n-1}$ (here C is a constant). Hence, an increase in the pressure results in the leading growth in the equilibrium constant of formation of the high-molecular polymer. If, for example, ethylene is polymerized at 800 K and a pressure 50 times greater than atmospheric (5 MPa), the equation for cal-

culating x_e will be as follows:

$$x_e + 0.6 \times 50 x_e^2 + 0.06 \times 50^2 x_e^3 + 0.04 \times 50^3 x_e^4 = 1$$

The solution of this equation is $x_e \approx 0.1$, i.e. the degree of conversion of the monomer will grow from 31 to about 90%. An equilibrium mixture obtained in polymerization at an increased pressure will contain (in mole fractions) 0.28 of the dimer, 0.14 of the trimer, and 0.48 of the tetramer. The growth in the content of the latter is especially significant (at atmospheric pressure its mole fraction is 0.01).

6.4.2. Liquid-Phase Oligomerization of Alkenes

The low-molecular polymerization of alkenes in the liquid phase is used to produce dimers, trimers, and tetramers of C_3-C_5 alkenes, some of the processes being employed in the industry. The studying of the oligomerization of vinyl monomers is also a stage in the analysis of industrially important processes of their high-molecular polymerization with the production of solid polymers.

It should be noted that the conditions $\Delta G = \Delta H - T\Delta S$ or $\Delta A = \Delta U - T\Delta S$ hold for any systems. In equilibrium, ΔG always equals zero if the temperature and pressure are constant, or $\Delta A = 0$ if the temperature and volume are constant. When considering oligomerization under isobaric-isothermal conditions, the following cases are possible.

(a) $\Delta H < 0$ and $\Delta S > 0$. Here we always have $\Delta G < 0$, and oligomerization is possible at any temperatures;

(b) $\Delta H < 0$ and $\Delta S < 0$. Here at low temperatures $\Delta G < 0$ and at high ones $\Delta G > 0$. Oligomerization is possible at temperatures below the limiting one T_{lim}, where $T_{lim} = \Delta H/\Delta S$;

(c) $\Delta H > 0$ and $\Delta S > 0$. Here ΔG will be positive at low temperatures and negative at high ones, i.e. oligomerization is possible at temperatures above the limiting one T_{lim};

(d) $\Delta H > 0$ and $\Delta S < 0$. Here ΔG is always positive, and oligomerization is impossible.

It should be indicated that cases (c) and (d) are of no interest because oligomerization proceeds with the evolution of heat ($\Delta H < 0$). The most frequent case for oligomerization is $\Delta S < 0$ characterized by case (b). This is why oligomerization can also be characterized by the quantity T_{lim}, but the latter quantity is used most frequently to characterize high-molecular polymerization.

The intricacy of calculations for liquid-phase processes is associated with the fact that most standard thermodynamic tables present the characteristics of substances in the state of an ideal gas at 0.1 MPa, and it is necessary to evaluate the thermodynamic functions for the liquid state from them. Below we shall restrict ourselves to calculations for liquids that are ideal solutions. The working relations have been substantiated in Sec. 2.6.

The heats of reactions in the liquid phase ΔH_{lq} can be determined from the heats of the gas-phase reaction ΔH, of condensation of the reactants ΔH^{cond} and vaporization of the products ΔH^{v}:

$$\Delta H = \Delta H^{cond} + \Delta H_{lq} + \Delta H^{v}$$

Below we compare the heats of gas-phase and liquid-phase low-molecular polymerization of *n*-1-butene to 1-octene and 1-dodecene:

	Heat of reaction at 300 K, kJ	
	gas-phase	liquid-phase*
$2C_4H_8 \rightarrow C_8H_{16}$	—82.4	—73.2
$3C_4H_8 \rightarrow C_{12}H_{24}$	—164.8	—143.5

* The heats of vaporization (in kJ/mol) are 22, 34, and 44 for butene, octene, and dodecene, respectively.

It should be noted that the following condition is observed for the reaction $nA \rightarrow A_n$:

$$\Delta H_{lq} = \Delta H + \frac{n-1}{2} \Delta H_M^v \qquad (6.31)$$

where ΔH_M^v is the molar heat of vaporization of the monomer.

Since $\Delta H < 0$, while $\Delta H_M^v > 0$, it is evident that $|\Delta H_{lq}| < |\Delta H|$, i.e. reactions in the gas phase proceed with a greater evolution of heat than in the liquid one. In both the gas and liquid phases, the heat of the consecutive attachment of a monomer unit remains virtually unchanged, which is depicted by the following data for oligomerization with the formation of 1-alkenes:

	Heat of reaction at 300 K, kJ	
	gas-phase	liquid-phase
$C_2H_4 + C_2H_4 \rightarrow C_4H_8$	—96	—89
$C_4H_8 + C_2H_4 \rightarrow C_6H_{12}$	—95	—88
$C_6H_{12} + C_2H_4 \rightarrow C_8H_{16}$	—94	—87
$C_8H_{16} + C_2H_4 \rightarrow C_{10}H_{20}$	—94	—87
$C_{10}H_{20} + C_2H_4 \rightarrow C_{12}H_{24}$	—94	—87
$C_4H_8 + C_4H_8 \rightarrow C_8H_{16}$	—82	—73
$C_8H_{16} + C_4H_8 \rightarrow C_{12}H_{24}$	—82	—73
$C_{12}H_{24} + C_4H_8 \rightarrow C_{16}H_{32}$	—82	—73

It is also easy to see that constant changes in the attachment of a monomer unit are also observed for ΔS of reactions in the gas or liquid phases.

It has been shown above that the changes in the Gibbs energy for the same reaction when it is conducted in the gas or in the liquid phase are identical if the temperatures of the phases are the same, namely, $\Delta G = \Delta G^{lq}$. This signifies that the data of standard thermodynamic tables for the gas phase can be used to find ΔG (but not ΔG°!), and liquid-phase reactions are characterized by the same quantities. We can omit the finding of ΔG for a gas reaction and

limit ourselves to the determination of the standard change in the Gibbs energy ΔG°. Having further calculated the gas-phase reaction equilibrium constant $K_p = \exp(-\Delta G^\circ/KT)$, we can easily go over to the equilibrium constant K_x^{lq} for the liquid-phase reaction that determines the mole fractions of the components in the liquid phase:

$$K_x^{lq} = \frac{K_p}{K_{p^\circ}} \tag{6.32}$$

In Eq. (6.32), K_{p° is determined by the saturated vapour pressures p_i° of the components at the temperature of the reaction. For oligomerization following the equation $nA \rightarrow A_n$, we obtain

$$K_x^{lq} = K_p \frac{(p^\circ A)^n}{p^\circ A_n} = \frac{K_x}{p^{n-1}} \frac{(p^\circ A)^n}{p^\circ A_n} \tag{6.33}$$

Since in the absence of a diluent, the total pressure in the system is

$$p = p_A + p_{A_n} = p_A^\circ x_A^{lq} + p_{A_n}^\circ x_{A_n}^{lq}$$

we have

$$K_x^{lq} = \frac{K_x}{(p_A^\circ x_A^{lq} + p_{A_n}^\circ x_{A_n}^{lq})^{n-1}} \frac{(p_A^\circ)^n}{p_{A_n}^\circ} \tag{6.34}$$

Since the saturated vapour pressure of a monomer is appreciably higher than the relevant quantity for its polymer, the equilibrium constant K_x^{lq} for a liquid-phase reaction is always larger than the equilibrium constant K_x for a gas-phase one. For example, for the dimerization of 1-butene, the ratio $p_A^\circ/p_{A_n}^\circ$ is 20-40, whereas the ratio K_x^{lq}/K_x has an order of magnitude of 10^3. This signifies that with a view to thermodynamic considerations, it is more preferable to conduct polymerization in the liquid phase. Even if in the gaseous phase the equilibrium degree of conversion of the monomer is not high, the reaction can be conducted with high degrees of conversion at the same temperature in the liquid phase.

6.4.3. High-Molecular Polymerization

For high-molecular polymerization $nA \rightarrow A_n$, the conditions substantiated in preceding sections are observed, namely,

$$\Delta H = n\Delta H_M, \quad \Delta S = n\Delta S_M$$

where ΔH_M and ΔS_M are the changes in the enthalpy and entropy when one monomer unit (A) is attached, n is the number of units in the polymer, ΔH_M and ΔS_M do not depend on n.

Now for the previously introduced limiting temperature of polymerization T_{lim} at which $\Delta G = 0$, we have

$$T_{lim} = \frac{\Delta H_M}{\Delta S_M}$$

The values of ΔH_M and ΔS_M were originally found by experimental measurements employing the methods of calorimetry and determination of the equilibrium concentrations of the monomer. In the calorimetric methods, the heats of combustion of the polymer $\Delta H_{c,P}$ and the monomer $\Delta H_{c,A}$ were measured. Next the calculations were performed using the obvious expression

$$\Delta H_M = \frac{1}{n}(n\Delta H_{c,A} - \Delta H_{c,P}) \tag{6.35}$$

The direct measurement of the heat of polymerization was also possible in a number of cases when this reaction was conducted in a calorimeter.

The method of measuring the equilibrium concentration of a monomer was found to be very successful. It enables one to find both ΔH_M and ΔS_M. We shall stop to substantiate it in greater detail to illustrate the thermodynamic analysis of high-molecular polymerization processes.

$$A_n^* + A \underset{k_d}{\overset{k_g}{\rightleftarrows}} A_{n+1}^*$$

Here A is a monomer, A_n^* and A_{n+1}^* are actively growing polymer particles with n or $n+1$ units, and k_g and k_d are the rate constants of polymer chain growth and depolymerization, respectively.

If n is large enough, then k_g and k_d do not depend on n. If thermodynamic equilibrium has been reached, this signifies that the rate of growth measured according to the using up of A should be equal to the rate of depolymerization. This condition written for the growing and depolymerizing molecules has the form

$$k_g c_A \sum_n^{\infty} c_{A_n^*} = k_d \sum_n^{\infty} c_{A_n^*}$$

where c is the concentration of the molecules.

The ratio of the rate constants k_g/k_d for the forward and reverse processes equals the equilibrium constant of polymerization. It depends neither on the concentration nor on n and is determined by the equilibrium concentration of the monomer:

$$K = \frac{k_g}{k_d} = \frac{1}{c_A}$$

Since in equilibrium reached from the initial state in which only the monomer was present, we have

$$\Delta G^\circ = -RT \ln K = RT \ln c_A = \Delta H^\circ - T\Delta S^\circ$$

then

$$\ln c_A = \frac{\Delta H^\circ}{R}\,\frac{1}{T} - \frac{\Delta S^\circ}{R}$$

Hence, having measured the equilibrium concentrations of the monomer c_A at several temperatures T, we plot a straight line in the coordinates $\ln c_A$ versus $1/T$. The ordinate intercept equals $-\Delta S^\circ/R$ and the slope of the line is $\Delta H^\circ/R$.

The concentrations of a monomer in equilibrium with a "live" (i.e. growing) polymer are very low and can be determined only by spectral methods of analysis. For example, the equilibrium concentration of styrene in the reaction system styrene-polystyrene is as follows:

Polymerization temperature, °C	100	110	120	130	150
$c_A \times 10^5$, mol/litre:					
in benzene	—	12	21	34	91
in cyclohexane	4	8	14	24	65

A growth in the temperature can be seen to increase the equilibrium concentration of the reactant and lower the equilibrium constant. But within the entire indicated temperature range, the concentration of the monomer does not exceed 0.001 mol/litre.

Naturally, owing to the errors in measuring the heats of the reactions, the number of monomer units in a polymer, and the concentrations of the monomer, the data of different investigators who determined ΔH_M and ΔS_M for the same reaction can differ substantially (up to 30-40%). In this connection, the reference data contained in various reviews are also not always consistent [6, 8].

Table 76. **Heats ΔH_M and Entropy Changes ΔS_M in Polymerization with the Formation of a Solid Partly Crystalline Polymer at 25 °C**

Monomer (state)	$-\Delta H_M$, kJ/mol of monomer unit	$-\Delta S_M$, J/(mol of monomer unit·K)
Ethylene (g)	88.7	159
Propylene (g)	82.0	184
Isobutene (g)	54.0	188
Vinyl chloride (g)	132.0	—
Vinylidene chloride (g)	100.0	—
Vinyl acetate (lq)	84	110
Butadiene (lq)	74	89
Isoprene (lq)	75	109
Chloroprene (lq)	68	—
Styrene (lq)	70	105
1-Methylstyrene (lq)	35	—
Acrylonitrile (lq)	77	—
Acrylamide (lq)	77	—
Methyl acrylate (lq)	78	—
Methyl methacrylate (lq)	54	117
Formaldehyde (g)	31	176
Ethylene oxide (g)	96	—
Cyclopropane (g)	0	−10

Nevertheless, we can recommend the data presented in Table 76 for thermodynamic analysis.

Measurements have also shown that both ΔH_M and ΔS_M depend only slightly on the temperature, at any rate the changes in these quantities with the temperature are smaller than the errors in their determination. This is illustrated, for example, by the data on the heats of polymerization presented in Table 77 [44].

Table 77. **Heats of Polymerization of Styrene and Methyl Methacrylate**

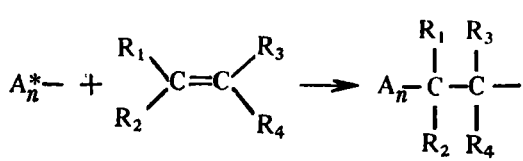
Monomer	Polymerization temperature, °C	Heat of polymerization $-\Delta H_M$, kJ/mol of monomer unit
Styrene	−60	67.3
	27	74.1
	74	68.6
	127	72.8
Methyl methacrylate	20	54.0
	77	54.4
	120	56.1
	125	54.0

Table 77 reveals that the data in Table 76 can also be used for temperatures substantially differing from 25 °C.

We shall not discuss here the possible causes of the differences in the polymerization heats and entropies [44,47]. We shall only note that the values of ΔS_M are less sensitive to the nature of the monomer than ΔH_M.

One can ask, however, whether it is possible to calculate ΔH_M and ΔS_M without resorting to an experiment or by using data of already performed investigations. Such calculations are quite valuable because the number of monomers subjected to polymerization is constantly growing, while a thermodynamic experiment is time-consuming. The following approach seems to be the simplest one.

Assume that a process in step n is described by the scheme:



We can evaluate the heat of this reaction by using the energies of the bonds being broken and the ones being formed. In accordance with the above scheme, one double bond in the monomer is replaced

by two single ones in the polymer. If $E_{C=C}$ and E_{C-C} are the energies of a double and single bonds in hydrocarbons, then the heat of the above step is

$$\Delta H_M = E_{C=C} - 2E_{C-C} \tag{6.36}$$

In a similar way, we can calculate the heats of polymerization when other double and triple bonds are opened (C=N, C=O, C=S, and so on) as the difference between the energies of the initial and the newly formed bonds. One must bear in mind, however, that the bond (binding) energies given in reference books have been obtained for molecules in the ideal gas state. Hence, calculations using known bond energies enable us to determine the heat of a hypothetic reaction in the gas phase. Nevertheless, it is simple to obtain data calculated in this way, and they are interesting as estimates of the real heats of polymerization. Table 78 presents bond energies and the calculated heats of polymerization.

Table 78. **Bond Energies and Heats of Polymerization of Selected Compounds in the Gas Phase***

Monomer structure	Bond energy, kJ/mol	Polymer structure	Bond energy, kJ/mol	Heat of polymerization, kJ/mol of monomer unit
C=C	423	C—C—	262	−101.4
C=O	628	C—O—	314	0
C≡C	759	C=C—	423	−74
C=N	618	C—N—	306	−6
C=S	493	C—S—	226	−59

* The values of the bond energies given by Pauling and Syrkin have been used.

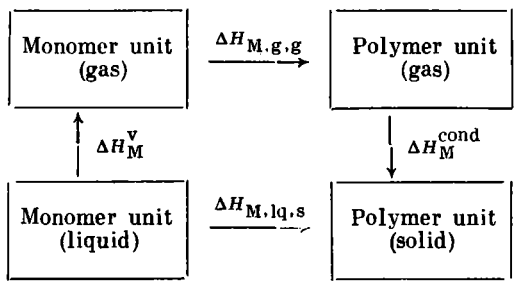
It should be noted that the values of the bond energies given by various authors differ quite substantially because of the use of different approaches in the intermediate calculation of the heat of atomization of graphite. If the heats measured for real polymerization and those calculated for hypothetic gas-phase polymerization are additionally compared (see Tables 76 and 78), the strong effect of the nature of the substituents at the vinyl group on ΔH_M becomes clear.

A number of investigations have been performed to explain the reasons of the differences between the experimental heats of polymerization and those calculated from the bond energies. Their results show these reasons to be (1) stabilization of the electrons in the monomer or polymer by the functional groups, (2) steric stresses in the polymerization of cyclic monomers, and (3) the formation of bonds between the molecules of the monomer or polymer (of the

hydrogen bond type) and solvation. The effect of substituents causing stabilization of the electrons is of the greatest significance.

It is difficult to take account of all the factors indicated above theoretically. This is why semi-empirical methods are used to calculate ΔH_M and ΔS_M.

Calculation of the Heats of Polymerization. The method of determining the heats of polymerization in the gas phase considered above can be improved by using the following cycle:



The heat of polymerization of a liquid monomer to a solid polymer $\Delta H_{M,lq,s}$ is calculated by the expression

$$\Delta H_{M,lq,s} = \Delta H_M^v + \Delta H_{M,g,g} + \Delta H_M^{cond}$$

The heat of monomer vaporization ΔH_M^v is determined accurately by refined experimental measurements; the heat of hypothetic polymerization in the gas phase $\Delta H_{M,g,g}$ is calculated as shown above from the bond energies, while the heat of "condensation" of a polymer unit ΔH_M^{cond} is estimated by any method. It is often assumed that $|\Delta H_M^{cond}| \approx |\Delta H_M^v|$.

The above scheme also allows us to find the heat of polymerization of a gaseous monomer to a solid polymer $\Delta H_{M,g,s}$ by the equation

$$\Delta H_{M,g,s} = \Delta H_{M,g,g} + \Delta H_M^{cond} \approx \Delta H_{M,g,g} - \Delta H_M^v$$

The same scheme enables us to find the heats of formation of each of the states since the heats of formation of the gaseous and liquid monomer are known. For a gaseous polymer unit, we have:

$$\Delta H_{f,P}^g = \Delta H_{f,A}^g + \Delta H_{M,g,g}$$

and for a solid polymer unit:

$$\Delta H_{f,P}^s = \Delta H_{f,A}^g + \Delta H_{M,g,g} + \Delta H_M^{cond}$$

Table 79 presents the heats of formation and polymerization for various compounds calculated on the basis of this scheme [47].

Table 79. **Heats of Vaporization of Monomers ΔH_M^v, Formation of Monomers $\Delta H_{f,A}$ and Polymers $\Delta H_{f,P}$, Heats of Polymerization $\Delta H_{M,lq,s}$ for Selected Compounds (All the Heats are in kJ/mol of monomer unit)***

Compound A (monomer)	$\Delta H_{f,A}$	ΔH_M^v	$-\Delta H_{f,P}$	$-\Delta H_{M,g,g}$ or $-\Delta H_{M,lq,s}$	
				calculated	experiment
Ethylene	52.3	13.4	41.0	93.3	88.7
Propylene	20.5	18.4	67.8	88.3	82.0
1-Butene	0	20.9	88.3	88.3	—
Isobutene	−16.7	20.5	102.1	85.8	54.0
Butadiene	110.0	20.9	−33.9	76.1	89.0
Isoprene	74.9	25.5	+3.6	78.2	109.0
Styrene	149.0	44.8	−67.3	85.8	105.0
1-Methylstyrene	118.0	47.7	−33.0	84.9	35.1
Vinyl chloride	21.8	20.5	74.9	93.3	132.0
Vinylidene chloride	2.1	27.2	109.2	111.3	100.0
Vinylidene fluoride	−331	17.1	416	84.9	125.5
Tetrafluoroethylene	−636	18.0	790	154	156
Nitroethylene	44.8	37.7	37.2	82.0	90.8
Acrylic acid	−333	46.0	397	63.2	77.4
Acrolein	−74.5	30.5	149	74.1	79.9
Acrylonitrile	184	32.6	−90	94.1	77.0
Ethylvinyl ether	−140	—	226	85.4	—
Vinyl acetate	−326	32.6	406	79.5	87.9
Methyl acrylate	−323	33.0	395	72.4	78.6
Methyl methacrylate	−341	36.0	429	87.9	54
Maleic anhydride	−412	44.0	506	96.2	58.6
Formaldehyde	−116	24.7	165	49.4	30.6
Acetaldehyde	−156	27.2	201	44.3	—
Ethylene oxide	−52.7	25.9	167	115	95
Styrene oxide	43.9	54.3	47.3	91	22.2
Tetrahydrofuran	−184	32.2	208	24.3	—
Cyclopropene	279	18.8	−106.3	172	116
Cyclopropane	52.7	20.9	65.7	118	—3
Cyclohexane	−123	33.0	131	8.4	34.7
Cyclooctane	−124	44.8	164	39.7	—
Allene	192	18.4	−39	153	—
Acetylene	228	17.6	−59	168	—
Acetonitrile	88	35.1	−69	19.2	—
Acetone	−213	31.8	245	28.4	—
Carbon monoxide	−110	7.1	129	18.4	—
Cyclooctatetraene	297	46.0	−63	234	—

* The calculations were performed by various investigators and are gathered in [47].

A comparison of the calculated and experimental heats of polymerization shows good coincidence of the data for vinyl monomers. Exceptions are (1) the polymerization of di-substituted ethylenes when both substituents are bound to one carbon atom (isobutene, vinylidene chloride), (2) polymerization resulting in the formation of polymers with very polar or volumetric substituents (methyl methacrylate), and (3) the polymerization of cyclic compounds with heteroatoms (maleic anhydride). At the same time, we can see that for most vinyl monomers the heat of polymerization ranges from —75 to —96 kJ/mol.

An interesting method of calculating the heats of polymerization was proposed by Flory [48]. He gave attention to the fact that there is an analogy between the reactions of hydrogenation of vinyl compounds and their polymerization. It consists in that two carbon atoms transfer from the trigonal (sp^2 hybridization in alkenes) to the tetrahedral (sp^3 hybridization in alkanes) form. This can result in correlation of the heats of hydrogenation and polymerization. Since in hydrogenation the bond C=C is replaced by two C—H bonds, while the energies of the C—H bonds in alkane chains are greater than those of the C—C bonds (the latter form in polymerization), then more heat evolves in hydrogenation than in polymerization. The following relation between the heat of hydrogenation ΔH_h and polymerization ΔH_M was found to exist:

$$\Delta H_M = \Delta H_h + B \tag{6.37}$$

The parameter B is determined by the nature of the substituents at the vinyl group. If the vinyl monomer has the structure $CH_2{=}CXY$, then when X≡Y≡H the parameter $B = 43.7$ kJ, if X is an alkyl and Y is hydrogen, $B = 38.6$ kJ. For example, the heat of hydrogenation of ethylene is $\Delta H_h = -137$ kJ. Let us use this value to calculate the heat of polymerization of ethylene by Eq. (6.37): $\Delta H_M = -137 + 43.7 = -89.3$ kJ/mol. This value is close to that determined experimentally (—95 kJ/mol).

It is much simpler to calculate the heats of hydrogenation than those of polymerization, and therefore the use of Flory's method is quite alluring. But the parameter B was found to vary very greatly when the substituents at the functional group change, and its value can be predicted only with a substantial error.

When calculating polymerization apparatus, we use the heats related to one kilogramme of polymer. These values are obtained from those given above by the conversion formula

$$q_{pr}\,(\text{in kJ/kg}) = \Delta H_M \frac{1000}{M}\,(\text{in kJ/mol})$$

where M is the molecular mass of the monomer.

Thus, if we use the values of ΔH_M contained in Table 76, we obtain $q_{pr} = -3168$ kJ/kg for ethylene, $q_{pr} = -1962$ kJ/kg for propylene, and so on.

Determining the Change in the Entropy in Polymerization. To determine the change in the entropy ΔS_M in polymerization, we can use a measurement of the equilibrium concentration of the monomer and perform our calculations by the equation $\ln c = (\Delta H^\circ/RT) - \Delta S^\circ/R$. Another possible method is based on the experimental determination of the limiting polymerization temperature T_{lim}. If we measure the rate of formation of the polymer or of consumption of the monomer, then near T_{lim} the rate being measured will be close to zero. Extrapolation of the plot of the rate against the temperature to the region of the zero rate will enable us to find T_{lim} with an accuracy within two or three kelvins. The further calculations are based on the following relations.

Since the rate of polymer growth is $w_g = k_g c_A \sum c_{A_n^*}$ and the rate of depolymerization is $w_d = k_d \sum c_{A_n^*}$, then taking into account the temperature dependence of the rate constants by the Arrhenius equation and the equality of w_g and w_d when $T = T_{lim}$, we find

$$K_{0,g} \exp\left(-\frac{E_g}{RT_{lim}}\right) c_A = k_{0,d} \exp\left(-\frac{E_d}{RT_{lim}}\right)$$

Consequently, having in view that the difference between the activation energies of the forward and reverse reactions equals the heat, we obtain:

$$T_{lim} = \frac{E_g - E_d}{R \ln (c_A k_{0,g}/k_{0,d})} = \frac{\Delta H_M}{R \ln c_A + R \ln (k_{0,g}/k_{0,d})} \qquad (6.38)$$

Moreover, by the theory of absolute reaction rates, $\ln (k_{0,g}/k_{0,d}) = \Delta S/R$, hence

$$\Delta H_M = RT_{lim} \ln c_A + RT_{lim} \Delta S_M$$

or

$$\Delta S_M = \frac{\Delta H_M}{T_{lim}} - R \ln c_A \qquad (6.39)$$

The third method of determining ΔS_M is based on calculating the entropies of polymers with involvement of the methods of statistical thermodynamics. This is a quite complicated task requiring the introduction of a number of assumptions. Thus, even at 0 K, the entropy of polymers does not equal zero because of the presence of an amorphous phase. Approximate estimates yield a value of about 5 J/mol for this "residual" entropy. By adopting this value, we can further calculate the entropy of a polymer by the conventional relations on the basis of measurements of the heats of phase tran-

sitions and the heat capacities of the polymers. The determination of ΔS_M and of the entropies of polymers from it has shown a considerably greater effect of the degree of crystallinity on the magnitude of the entropy, which can be seen from the data in Table 80.

Table 80. **Entropy of a Polymer Depending on Its Degree of Crystallinity**

Polymer	Degree of crystallinity, %	Entropy S, J/(mol of monomer unit·K)
Polyethylene	0	62
	58	52
	79	49
	100	46
Isotactic polypropylene	0	81
	48	81
	100	42
Atactic polypropylene	16	79
	100	63
Polyisobutene	—	129
cis-Polybutadiene	—	115
trans-Polybutadiene	—	98
Polyisoprene	—	128
Polymethylmethacrylate	—	144
Polyhydroxymethylene	100	43
Polyvinylidene chloride	—	71
Polytetrafluoroethylene	100	101

A glance at the table, however, reveals that the entropy is affected the most by the nature of the monomer.

The values of ΔS_M for polymerization are given in Table 76. These values change for various monomer units, but to a considerably lower extent than ΔH_M. For the overwhelming number of polymerization reactions, the values of ΔS_M are negative, while for vinyl monomers they are within the quite narrow interval from —110 to —190 J/(mol·K). The values of ΔS_M for the polymerization of C=O-containing monomers are also within this interval. The magnitude of ΔS_M is somewhat lower for polydienes (by 10-20 units).

Calculation of the Change in the Gibbs Energy, Equilibrium Constant, and Limiting Polymerization Temperature. If the heats and changes in the entropy in polymerization have been established, the change in the Gibbs or Helmholtz energy, the equilibrium constant, and in the limiting temperature is calculated by known relations ($\Delta G_M = \Delta H_M - T\Delta S_M$, $\Delta G^\circ_M = -RT \ln K$, and $T_{lim} = \Delta H_M/\Delta S_M$), and no difficulties are encountered here. It must only be stressed that for high-molecular polymerization, the equilibrium constant is the ratio of the rate constants of the polymer

chain growth and depolymerization:

$$K = \frac{k_g}{k_d}$$

The considerable evolution of heat in polymerization leads to the fact that within a large temperature interval ΔG_M is negative, i.e. thermodynamic restrictions are absent. To analyse the effect of the temperature on the thermodynamic probability of conducting polymerization, one must compare the signs of the quantities ΔH_M and ΔS_M. For most polymerization processes ΔH_M and ΔS_M are negative (see Table 76). Consequently, such processes are possible at temperatures below a certain limiting one. An exception is the polymerization of cyclic hydrocarbons with a stressed ring (cyclopropane), for which $\Delta S_M > 0$. The concept of T_{lim} loses its meaning for such systems.

Table 81. **Gibbs Energies ΔG_M, Equilibrium Constants K, and Limiting Polymerization Temperatures for Selected Monomers**

Monomer	$-\Delta G_M$, kJ/mol of monomer unit	K, m³/kmol at 300 K	T_{lim}, K
Ethylene	56	10^{10}	558
Propylene	43	10^{10}	446
Isobutene	18	10^{4}	320
Tetrafluoroethylene	122	10^{20}	—
Vinylidene chloride	—	—	410
Styrene	56	10^{10}	667
Butadiene	48	40	—
Isoprene	48	10^{9}	—
Methylmethacrylate	20-50	10^{4}	—

Table 81 gives the values of ΔG_M, the equilibrium constants, and the limiting temperatures for a number of polymerization processes [44, 47, 48].

It is obvious that the equilibrium of polymerization conducted at moderate ($\approx$300 K) temperatures is shifted greatly in the direction of the polymer molecules, and low temperatures are favourable from thermodynamic considerations. The thermodynamic restrictions will tell only at temperatures that are high for polymerization.

In this connection, the calculation of the equilibrium compositions for polymerization conducted at moderate temperatures is only of a theoretical interest.

However, the thermodynamic analysis of the equilibrium of intermediate steps (the principle of detailed equilibrium) is employed for studying the distribution of a product by molecular mass, for determination of the rate constants of reverse reactions from the constants of the forward ones, etc. Let us consider the thermodynamic analysis of the steps of high-molecular polymerization in the same way as we did above for oligomerization.

Thermodynamic Analysis of the Steps of High-Molecular Polymerization. When treating oligomerization, we advanced a method for calculating the amounts of the oligomers. For high-molecular polymerization, thermodynamic analysis enables us to establish important characteristics of polymers and polymerization. Such an analysis was given for the first time by Tobolsky and Eisenberg [49].

Below we shall consider the thermodynamics of polymerization steps proceeding without an initiator (I) and with one (II) by the schemes:

$$\left.\begin{array}{ll} A_1 + A_1 \rightarrow A_2 & K_2 = [A_2]/[A_1]^2 \\ A_1 + A_2 \rightarrow A_3 & K_3 = [A_3]/[A_1]\,[A_2] \\ A_1 + A_{n-1} \rightarrow A_n & K_n = [A_n]/[A_1]\,[A_{n-1}] \end{array}\right\} \quad \text{(I)}$$

$$\left.\begin{array}{ll} YZ + A_1 \rightarrow YAZ & K_1' = [YAZ]/[A_1]\,[YZ] \\ YAZ + A_1 \rightarrow YA_2Z & K_2' = [YA_2Z]/[A_1]\,[YAZ] \\ YA_{n-1}Z + A_1 \rightarrow YA_nZ & K_n' = [YA_nZ]/[A_1]\,[YA_{n-1}Z] \end{array}\right\} \quad \text{(II)}$$

Here A_1 is a monomer, K_i and K_i' are equilibrium constants, $[A_i]$ is the concentration of substance A_i, and YZ is an initiator between whose groups Y and Z the monomer units become implanted.

The use of the constants K_x and the mole fractions of the components loses all meaning for polymerization. It is better to employ the kinetic approach and consider each equilibrium constant as the ratio of the rate constants for the forward and reverse reactions, and to measure the concentration by the number of moles per unit mass of the reaction mixture.

Polymerization without an Initiator. From the expressions for the equilibrium constants, we have

$$[A_2] = K_2\,[A_1]^2$$

$$[A_3] = K_3\,[A_1]\,[A_2] = K_2K_3\,[A_1]^3$$

$$\cdot\;\cdot\;\cdot$$

$$[A_n] = K_n\,[A_1]\,[A_{n-1}] = K_2K_3\ldots K_n\,[A_1]^n$$

The total concentration of all the polymer molecules is

$$[P] = [A_2] + [A_3] + \ldots + [A_n] = K_2\,[A_1]^2 + K_2K_3\,[A_1]^3 + \ldots + K_2K_3\ldots K_n\,[A_1]^n = K_2\,[A_1]^2\,\{1 + K_3\,[A_1] + K_3K_4[A_1]^2 + \ldots + K_3K_4\ldots K_n\,[A_1]^{n-2}\}$$

It is also easy to find the concentration of the monomer units A bound into the polymer molecules $[A]_{\text{in polymer}}$ ($n \geqslant 2$):

$$[A]_{\text{in polymer}} = \sum_{n=2}^{\infty} n\,[A_n] = \sum_{n=2}^{\infty} nK_2K_3 \ldots K_n\,[A]^n$$

The ratio of $[A]_{\text{in polymer}}$ to $[P]$ yields the mean degree of polymerization Π:

$$\Pi = \frac{[A]_{\text{in polymer}}}{[P]}$$

$$= \frac{\sum_{n=2}^{\infty} nK_2K_3 \ldots K_n\,[A_1]^n}{K_2\,[A_1]^2\{1 + K_3\,[A_1] + K_3K_4\,[A_1]^2 + \ldots + K_3K_4 \ldots K_n\,[A_1]^{n-2}\}}$$

In the thermodynamic analysis of oligomerization, we showed that at substantial values of n, the quantities ΔG, ΔH, ΔS, and the equilibrium constants stop depending on n. We can therefore consider simplifications of the obtained relations based on two approximations:

1. The equilibrium constants of all the steps except initiation are the same. In this case, the polymerization process by scheme I is characterized by two constants, namely, K_2 and K_3; here $K_3 = K_4 = \ldots = K_n$. We have

$$[P] = K_2\,[A_1]^2\{1 + K_3\,[A_1] + K_3^2[A_1]^2 + \ldots + K_3^{n-2}\,[A_1]^{n-2}\}$$

$$= \frac{K_2\,[A_1]^2}{1 - K_3\,[A_1]}$$

(because the series of numbers $1 + a + a^2 + \ldots \approx 1/(1 - a)$ when $a < 1$), and

$$[A]_{\text{in polymer}} = 2K_2\,[A_1]^2 + 3K_2K_3\,[A_1]^3 + \ldots + nK_2K_3^{n-2}\,[A_1]^n$$

$$= K_2\,[A_1]^2\{2 + 3K_3\,[A_1] + \ldots + nK_3^{n-2}\,[A_1]^{n-2}\} = \frac{K_2\,[A_1]^2}{(1 - K_3\,[A_1])^2}$$

$$\left(\text{because } \sum_{i=2}^{n} iK_3^{i-2}\,[A_1]^{i-2} \approx \frac{1}{1 - K_3\,[A_1]^2}\right)$$

Hence,

$$\Pi = \frac{1}{1 - K_3\,[A_1]}$$

When $\Pi \gg 1$, the previously used condition that $K_3 \approx [A_1]^{-1}$ is satisfied.

The initial concentration of the monomer $[A_1]_0$ equals the sum of its equilibrium concentration $[A_1]$ and the concentration of the

monomer in the polymer $[A]_{\text{in polymer}}$:

$$[A_1]_0 = [A_1] + [A]_{\text{in polymer}}$$

Consequently,

$$[A_1]_0 = [A_1] + \frac{K_2 [A_1]^2}{1 - K_3 [A_1]^2}$$

If in this equation we express $[A_1]$ in terms of Π, we find

$$\Pi = \left(\frac{[A_1]_0 K_3^2}{K_2} - \frac{K_3}{K_2} \right)^{1/2}$$

2. The equilibrium constants of all the steps are the same. Here $K_2 = K_3 = \ldots = K_n = K$, and all the expressions obtained for the first case hold if the subscripts on the equilibrium constants are dropped.

Polymerization with an Initiator. Scheme II characterizes matters when the initiator YZ participates in equilibrium steps. Whether or not this is true can be established experimentally from the concentration of the initiator prior to the reaction and in an equilibrium mixture. Moreover, scheme II presumes the presence of a certain amount of initiator in the growing ("live") polymer molecules.

The system of equations relating the equilibrium concentrations is as follows:

$$[YAZ] = K_1' [YZ] [A_1]$$
$$[YA_2Z] = K_2' [YAZ] [A_1] = K_1' K_2' [YZ] [A_1]^2$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$[YA_nZ] = K_n' [YA_{n-1}Z] [A_1] = K_1' K_2' \ldots K_n' [YZ] [A_1]^n$$

If we have in view that the compound YA_iZ further forms the polymer molecule A_i, we have $[A_i] = [YA_iZ]$.

We shall consider that the equilibrium constants of all the growth steps are the same: $K_2' = K_3' = \ldots = K_n'$. Hence

$$[YA_nZ] = K_1' K_2'^{n-1} [YZ] [A_1]^n$$

The following expression holds for the concentration of all the polymer molecules:

$$[P] = [A_2] + [A_3] + \ldots + [A_n] = K_1' K_2' [YZ] [A_1]^2$$
$$+ K_1 K_2'^2 [YZ] [A_1]^3 + \ldots + K_1' K_2'^{n-1} [YZ] [A_1]^n$$
$$= K_1' K_2' [YZ] [A_1]^2 \{1 + K_2' [A_1] + K_2'^2 [A_1]^2 + \ldots + K_2'^{n-2} [A_1]^{n-2}\}$$
$$= \frac{K_1' K_2' [YZ] [A_1]}{1 - K_2' [A_1]}$$

The concentration of the monomer units in the polymer molecules is

$$[A]_{\text{in polymer}} = \sum_{n=2}^{\infty} n\,[A_n] = \sum_{n=2}^{\infty} nK_1'K_2'^{n-1}[A_1]^n[YZ] = \frac{K_1'K_2'[YZ][A_1]}{(1-K_2'[A_1])^2}$$

Therefore, the mean degree of polymerization is

$$\Pi = \frac{[A]_{\text{in polymer}}}{[P]} = \frac{1}{1-K_2'[A_1]}$$

Taking into account that the equilibrium concentrations of the monomer and initiator are related to the initial concentrations (subscript "0") by the expressions:

$$[A_1]_0 = [A_1] + [A]_{\text{in polymer}} = [A_1]\,\frac{1+K_1'[YZ]}{\Pi^2}$$

$$[YZ]_0 = [YZ] + [P] = [YZ]\,(1 + K_1'K_2'[A_1]\,\Pi)$$

we also obtain

$$\Pi = \frac{[A_1]_0 - [A_1]}{[YZ]_0 - [YZ]}$$

In the second case, the same relations hold, but $K_1' = K_2' = K$.

The applications of these relations to various types of polymerization have been generalized by Sawada [44].

The values of K_1 and K_2 for vinyl compounds were determined by measuring Π. For methylmethacrylate, they equalled about 3×10^{-5} and 3, respectively.

The polymerization of styrene and its homologues initiated by lithium butyl is consistent with the equation for Π ($K_1 = K_2 = K$). Here the dependence of K on the nature of the solvent has been noted (Fig. 25); the slopes of the lines for different solvents are the

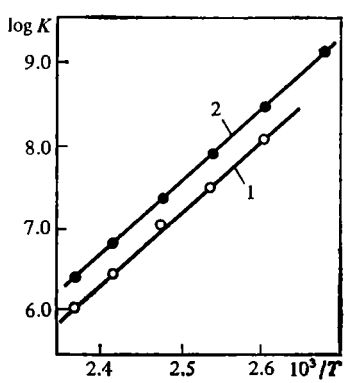


Fig. 25. Temperature dependence of the equilibrium constant of styrene polymerization in various solvents: *1*—in benzene; *2*—in cyclohexane

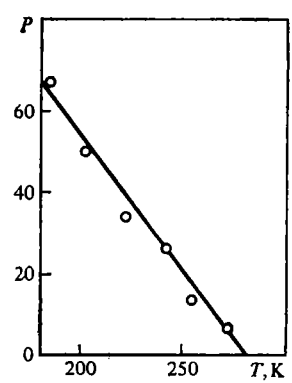


Fig. 26. Temperature dependence of the mean equilibrium degree of polymerization Π of 1,3-dioxolane

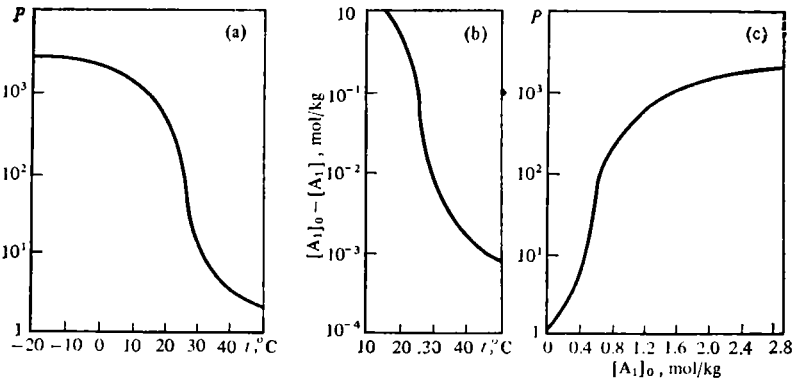


Fig. 27. Influence of the temperature t and initial concentration of the monomer $[A_1]_0$ on the equilibrium concentration of the monomer $[A_1]$ and the degree of polymerization Π for the polymerization of 1-methylstyrene. The initial concentration of the initiator was 0.001 mol/kg:

a—Π vs. t for $[A_1]_0 = 2.5$ mol/kg; *b*—$[A_1]_0 - [A_1]$ vs. t for the same initial monomer concentration; *c* — Π vs. $[A_1]_0$ for $t = 5.6$ °C

same (from —30 to —35 kJ/mol). We have already indicated that the relation $K = f(T)$ can also be used to find ΔS. For the homologues of styrene, ΔS ranges from —105 to —130 J/(mol·K). Figures 26 and 27 illustrate the effect of various factors on the degree of polymerization and are consistent with the developed theory.

Polymerization with ring opening has been studied very thoroughly, chiefly as applied to the production of polycaprolactam. The following conditions were found to hold:

$$\Pi = \frac{[A_1]_0 - [A_1]}{[YZ]_0 - [YZ]}, \quad [YZ]_0 = [YZ](1 - K[A_1]\Pi)$$

It was found by measuring Π and the concentrations of the monomer and initiator that

$$K'_1 = \exp\left(\frac{28.6}{R}\right)\exp\left(-\frac{9360}{RT}\right)$$

$$K'_2 = \exp\left(-\frac{29.4}{R}\right)\exp\left(\frac{16\,850}{RT}\right)$$

(Here in the exponents, the change in the entropy ΔS is divided by R, and the decrease in the enthalpy ΔH in J is divided by RT).

The polymerization of aldehydes has also been studied in sufficient detail. In the production of polyhydroxymethylene from formaldehyde, the equilibrium pressure p of the monomers was measured, and the equation

$$RT \ln p = \Delta H^\circ + T\Delta S^\circ$$

was used to find ΔH° and ΔS°. According to various data, ΔH° ranges from -55 to -70 kJ/mol, and ΔS° ranges from -130 to -175 J/(mol·K).

In analysing the steps of radical or ion polymerization, thermodynamic analysis enables us to find their heats, and from the latter—the differences of the activation energies ($\Delta H_{12} = E_1 - E_2$) or even the activation energies. The heats and activation energies of polymerization steps are given in [44, 47-52]. Let us consider as an illustration the steps of producing polyethylene.

The initiation of ethylene polymerization includes the step of chain growth (the formation of an active growing radical):

$$R\cdot + C_2H_4 \rightarrow R{-}C_2H_4\cdot$$

Calculations reveal that if $R\cdot \equiv H\cdot$, then $\Delta G^\circ = -141$ kJ, $\Delta H^\circ = -166$ kJ; if $R\cdot \equiv CH_3\cdot$, then $\Delta G^\circ = -70$ kJ, $\Delta H^\circ = -114$ kJ; and if $R\cdot \equiv C_2H_5$, then $\Delta G^\circ = -108$ kJ, $\Delta H^\circ = -108$ kJ.

If $R\cdot$ is *n*-hexyl or a more high-molecular radical, then ΔG° and ΔH° stop depending on the molecular mass of $R\cdot$ and are -51 and -94 kJ/mol of C_2H_4, respectively. These values coincide with the values of ΔG° and ΔH° for gas-phase polymerization: $n\text{-}C_2H_5 \rightarrow (C_2H_4)_n$.

It is clear that growth of the chain is possible thermodynamically within a broad range of temperatures. The reaction of chain transfer of a hydrocarbon with the formation of a tertiary radical is also probable thermodynamically

$$n\cdot C_{20}H_{41}\cdot + C_3H_8 \rightarrow n\text{-}C_{20}H_{42} + (CH_3)_2CH\cdot$$
$$(\Delta G^\circ = -16\ \text{kJ},\quad \Delta H^\circ = -18\ \text{kJ})$$
$$n\text{-}C_{20}H_{41}^{\cdot} + (CH_3)_3CH \rightarrow n\text{-}C_{20}H_{42} + (CH_3)_3C\cdot$$
$$(\Delta G^\circ = -28\ \text{kJ},\quad \Delta H^\circ = -30\ \text{kJ})$$

Chain transfer with the formation of an *n*-alkyl radical, on the other hand, is much less probable thermodynamically. An example is the reaction

$$n\text{-}C_{20}H_{41}^{\cdot} + n\text{-}C_{10}H_{22} \rightarrow n\text{-}C_{20}H_{42} + n\text{-}C_{10}H_{21}\cdot$$
$$(\Delta G^\circ = 0,\quad \Delta H^\circ = 0)$$

At low temperatures, the reaction of detachment of a hydrogen atom from the radical is excluded:

$$n\text{-}C_{20}H_{41}\cdot \rightarrow n\text{-}C_{20}H_{40} + H\cdot$$
$$(\Delta G^\circ = 140\ \text{kJ},\quad \Delta H^\circ = 172\ \text{kJ})$$

Breaking of the chain is possible because of the reactions between two radicals:

$$2R\cdot \rightarrow R{-}R,\quad R_1\cdot + R_2\cdot \rightarrow \text{alkene} + \text{alkane}$$

For both reactions, ΔG° is below -210 kJ. But the high evolution of heat (over 220 kJ) requires the participation of an inert molecule (wall) for absorbing the energy.

Thermodynamic analysis also allows us to consider the effect of the pressure on the results of polymerization. From the conditions of polymerization equilibrium $dG_{\text{polymer}} = dG_{\text{monomer}}$ when T, p are constant and from the expression $dG_i = -S_i\,dT + v_i\,dp$, it follows that

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta v} = \frac{\Delta H}{T\Delta v} \tag{6.40}$$

Condition (6.40) is an analogue of the Clausius-Clapeyron equation.

With a relatively slight relation between T and p, we have

$$\frac{dp}{dT} \approx \frac{\Delta p}{\Delta T}, \quad \Delta T = \frac{T \Delta v \Delta p}{\Delta H}$$

For the formation of polyethylene, $\Delta v < 0$, $\Delta H < 0$, and $\Delta T > 0$ with a growth in the pressure; the value of $\Delta v/\Delta H$ is about 1.4 cm^3/kJ. This signifies that the temperature of equilibrium between the monomer and polymer grows with an increasing pressure. An increase in the pressure raises T_{11m} and makes it possible to conduct polymerization at higher temperatures, although it should be noted that the conducting of industrial polymerization at high pressures ($\approx$ 100 MPa) is associated with the surmounting of kinetic difficulties. Since

$$\left(\frac{\partial \Delta G^\circ}{\partial p}\right)_T = \Delta v \text{ and } \Delta G^\circ = -RT \ln K = RT \ln [A_1]$$

then

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta v}{RT} \text{ or } \left(\frac{\partial \ln [A_1]}{\partial p}\right)_T = \frac{\Delta v}{RT}$$

At high pressures, ΔG becomes more negative, and the thermodynamic probability of the reaction grows.

6.4.4. Copolymerization

We shall limit ourselves to a treatment of the reaction of two monomers. Assume that a copolymer forms from the monomers M_1 and M_2. Here the following four reactions of chain growth are possible, with the chain terminating in the monomer unit M_1—M_1— or M_2—M_2—(—M_1— or —M_2—):

$$-M_1- + M_1 \rightleftarrows -M_1-M_1- \quad \text{(reaction 1-1)}$$
$$-M_1- + M_2 \rightleftarrows -M_1-M_2- \quad \text{(reaction 1-2)}$$
$$-M_2- + M_1 \rightleftarrows -M_2-M_1- \quad \text{(reaction 2-1)}$$
$$-M_2- + M_2 \rightleftarrows -M_2-M_2- \quad \text{(reaction 2-2)}$$

Each of these reactions is characterized by its heat (ΔH_{11}, ΔH_{12}, ΔH_{21}, ΔH_{22}), change in entropy (ΔS_{11}, ΔS_{22}, ΔS_{12}, ΔS_{21}), and Gibbs energy, and by its equilibrium constant. Owing to the analogy of reactions 1-2 and 2-1, we can assume that $\Delta H_{12} \approx \Delta H_{21}$, $\Delta S_{12} \approx \Delta S_{21}$, and $\Delta G_{12} \approx \Delta G_{21}$.

If the obtained copolymer contains N_1 units of the first and N_2 units of the second monomer, the total number of monomer units will be $N_0 = N_1 + N_2$.

We shall denote the number of monomer bonds by N_{11}, N_{12}, N_{21}, and N_{22}, but since the probability of reactions 1-2 and 2-1 is the same, then $N_{12} \approx N_{21}$.

The monomer units M_1 participate in the bonds M_1—M_1, M_1—M_2, and M_2—M_1. Their total number is

$$N_1 = N_{11} + \frac{N_{12} + N_{21}}{2} = N_{11} + N_{12}, \quad N_{11} = N_1 - N_{12}$$

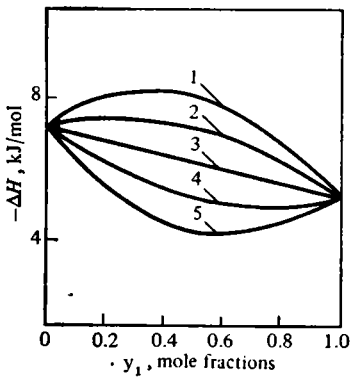


Fig. 28. Heat of copolymerization ΔH versus the content of the monomer M_1 in the copolymer y_1 at various values of z_H (in kJ/mol): *1*— +80; *2*— +40; *3*—0; *4*— —40; *5*— —80

Similarly, for the number of M_2 units, we find

$$N_2 = N_{22} + N_{12} \text{ or}$$

$$N_{22} = N_2 - N_{12}$$

The following expression holds for the summary copolymerization process characterized by the quantities ΔH, ΔS, and ΔG:

$$\Delta H = \frac{N_{11}}{N_0}\Delta H_{11} + \frac{N_{22}}{N_0}\Delta H_{22} + \frac{2N_{12}}{N_0}\Delta H_{12} = \frac{N_1}{N_0}\Delta H_{11} + \frac{N_2}{N_0}\Delta H_{22} + \frac{N_{12}}{N_0} \times (2\Delta H_{12} - \Delta H_{11} - \Delta H_{22})$$

We can consider the ratios $N_1/N_0 = y_1$ and $N_2/N_0 = y_2$ as the probabilities of the presence of M_1 and M_2 in the copolymer. Hence, the probability of the complex event—the presence in the copolymer of the unit M_1—M_2, is $y_{12} = y_1 y_2$, or

$$\frac{N_{12}}{N_0} = \frac{N_1}{N_0}\frac{N_2}{N_0}$$

Consequently,

$$\Delta H = y_1\Delta H_{11} + y_2\Delta H_{12} + y_1 y_2 (2\Delta H_{12} - \Delta H_{11} - \Delta H_{22})$$

The quantity $2\Delta H_{12} - \Delta H_{11} - \Delta H_{22}$ is designated by z_H and is known as the copolymerization parameter. Hence

$$\Delta H = y_1\Delta H_{11} + y_2\Delta H_{22} + y_1 y_2 z_H \tag{6.41}$$

It is clear from Eq. (6.41) that depending on the value of z_H, that of ΔH can be either larger or smaller than each of the quantities ΔH_{11} and ΔH_{22} (Fig. 28).

For example, the following data have been obtained for the copolymerization of methylmethacrylate with styrene [50]:

Fraction of methylmethacrylate in polymer y_1	1	0.65	0.50	0.35	0.21	0
Heat of copolymerization ΔH, kJ/mol . . .	55.2	64.2	65.1	68.6	70.2	69.2
Heat of reactions 1-2 and 2-1, ΔH_{12}, kJ/mol	—	67.5	66.5	69.0	71.0	—

The heat of copolymerization can be seen to pass through a gently sloping maximum. With a substantial change in ΔH, the heat of step $1 \rightarrow 2$ (or $2 \rightarrow 1$) is only slightly affected by a change in the composition: with account taken of the measurement errors, ΔH_{12} is constant and close to the greater of the heats ΔH_{11} or ΔH_{22}.

The change in the copolymerization entropy can be evaluated by a similar relation, but account must be taken of the additional contributions due to the formation of a glassy state, a change in the configuration, and mixing. The first two contributions are negligibly small [51]. For the last one, we can write (by analogy with the calculation of the entropy of mixing of ideal gases):

$$\Delta S_{\text{mix}} = -R\,(y_1^{\cdot} \ln y_1 + y_2^{\cdot} \ln y_2)$$

where $y_i^{\cdot}$ is the probability of appearance of the unit M_i—M_i.

Calculations have shown ΔS_{mix} to amount to 2-7 J/(mol·K), which does not exceed 5% of the total change in the entropy [48]. Hence, by analogy with ΔH [Eq. (6.41)], we find:

$$\Delta S = y_1 \Delta S_{11} + y_2 \Delta S_{22} + y_1 y_2 z_S \tag{6.42}$$

$$\Delta G = y_1 \Delta G_{11} + y_2 \Delta G_{22} + y_1 y_2 z_G \tag{6.43}$$

The nature of the dependences of ΔS and ΔG on the composition of the copolymer is the same as for ΔH (see Fig. 28).

When performing thermodynamic analysis of copolymerization, having in view that

$$K_{11} = \frac{[M_1]_n}{[M_{1,\,n-1}]\,[M_1]}, \quad K_{12} = \frac{[M_1 - M_2]}{[M_1]\,[M_2]}$$

Tobolsky and Owen [49] found that the total number of monomer molecules in a copolymer (the calculations are similar to those described above) is

$$N_0 = \frac{K_1'\,[M_1] + K_2'\,[M_2]}{1 - (K_1\,[M_1] + K_2\,[M_2])}$$

where K_1' and K_2' are the equilibrium constants of the initiation steps ($M_1 \rightleftarrows M_1^*$, $M_2 \rightleftarrows M_2^*$), while K_1 and K_2 are the equilibrium constants of the copolymer growth steps ($C + M_1 \rightleftarrows CM_1$, $C + M_2 \rightleftarrows CM_2$, where C stands for the copolymer).

The number of monomer units in the copolymer is

$$W = \frac{K_1'\,[M_1] + K_2'\,[M_2]}{\{1 - (K_1\,[M_1] + K_2\,[M_2])\}^2}$$

Therefore, the mean degree of copolymerization is

$$\Pi = \frac{N_0}{W} = \{1 - (K_1\,[M_1] + K_2\,[M_2])\}^{-1} \tag{6.44}$$

The following expression holds for the mole fraction of the first monomer in the copolymer:

$$x_1 = \frac{[M_1]_{\text{copol}}}{[M_1]_{\text{copol}} + [M_2]_{\text{copol}}} = \frac{K_1\,[M_1]}{K_1\,[M_1] + K_2\,[M_2]} \tag{6.45}$$

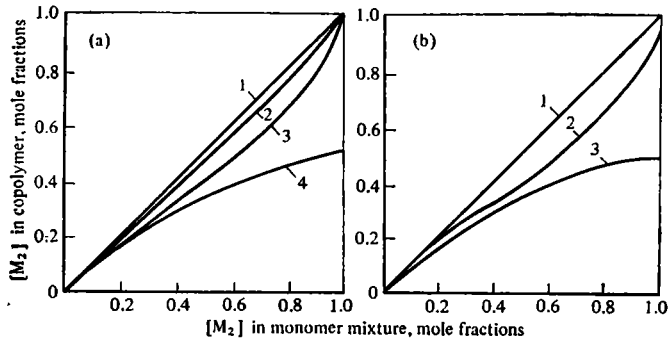


Fig. 29. Composition of a copolymer versus the content of the monomer in an equilibrium mixture for different temperatures (*a*) and initial compositions (*b*): (*a*): *1*—0 K; *2*—273 K; *3*—323 K; *4*—373 K; (*b*): *1*—$[M_1] + [M_2] = 1{,}0$; *2*—0.1; *3*—0.01

while for the change in the monomer concentration from the initial one $[M_1]_0$ to the equilibrium one, we have

$$[M_1]_0 = [M_1]\left\{1 + \frac{K_1(K_1'[M_1] + K_2'[M_2])\,\Pi^2}{K_1[M_1] + K_2[M_2]}\right\} \tag{6.46}$$

If $K_1' = K_1$ and $K_2' = K_2$, then

$$[M_1]_0 = [M_1](1 + K_1\Pi^2)$$
$$[M_2]_0 = [M_2](1 + K_2\Pi^2)$$

The above expressions allow us to find ΔH, ΔS, ΔG, the copolymerization equilibrium constants, the equilibrium concentrations of the monomers, and the composition of the copolymer. It follows from them that three situations are possible, namely, a growth in the monomer content in the initial mixture leads to a growth in its content in the copolymer; the latter quantity passes through a maximum or minimum. Which of these situations is realized in a specific case can be established from the values of the thermodynamic functions and the above expressions.

The effect of the temperature and the initial composition of the mixture on the equilibrium concentrations of the monomer in the free state and in the polymer is depicted in Fig. 29.

6.4.5. Polycondensation

Polycondensation reactions proceed with the formation of a growing high-molecular compound and the separation of a simple molecule (water, hydrogen chloride, etc.). The thermodynamic calculations of these reactions can be performed by employing the approach used for polymerization processes.

Let us consider high-molecular condensation following the scheme

$$\begin{array}{ll} M_1 \rightleftarrows M_1^* & K_1 = [M_1^*]/[M_1] \\ M_1^* + M_1 \rightleftarrows M_2^* + H_2O & K_2 = [M_2^*]\,[H_2O]/[M_1]^2 \\ M_2^* + M_1 \rightleftarrows M_3^* + H_2O & K_3 = [M_3^*]\,[H_2O]/[M_2^*]\,[M_1] \\ \cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots \\ M_{n-1}^* + M_1 \rightleftarrows M_n^* + H_2O & K_n = [M_n^*]\,[H_2O]/[M_{n-1}^*]\,[M_1] \end{array}$$

We shall express the concentrations of each of the polymer molecules by using the equations of the equilibrium constants. We shall have in view that the concentrations of the active particles M^* equal those of the polymer molecules: $[M_i^*] = [M_i]$. We obtain

$$\begin{array}{l} [M_2] = K_2\,[M_1]^2/[H_2O] \\ [M_3] = K_3\,[M_2]\,[M_1]/[H_2O] = K_2K_3\,[M_1]^3/[H_2O]^2 \\ \cdots\quad\cdots\cdots\cdots\quad\cdots\cdots\cdots \\ [M_n] = K_n\,[M_{n-1}]\,[M_1]/[H_2O] = K_2K_3\ldots K_n\,[M_1]^n/[H_2O]^{n-1} \end{array}$$

The total concentration of the polymer molecules is

$$N = \sum_{n=2}^{\infty} K_n\,[M_{n-1}]\,[M_1]/[H_2O]$$

$$= (K_2\,[M_1]^2/[H_2O])\left(1 + \frac{K_3\,[M_1]}{[H_2O]} + \cdots + \frac{K_3K_4\ldots K_n}{[H_2O]^{n-2}}\right)$$

This expression can be simplified if we assume that as for polymerization, $K_3 = K_4 = \ldots = K$ and denote $K_2\,[M_n]^2/[H_2O]$ by a. Hence

$$N = a\left(1 + \frac{K_3\,[M_1]}{[H_2O]} + \frac{K_3^2\,[M_1]^2}{[H_2O]^2} + \cdots\right)$$

$$= a\Big/\left(1 - \frac{K_3\,[M_1]}{[H_2O]}\right) \equiv a\Big/\left(1 - \frac{K\,[M_1]}{[H_2O]}\right)$$

Under these conditions, the total concentration of the monomer units in the polymer is

$$W = \sum_{n=2}^{\infty} n\,\frac{K^{n-1}}{[H_2O]^{n-1}}\,[M_1]^n = \frac{a}{\left(1 - \frac{K\,[M_1]}{[H_2O]}\right)^2}$$

Therefore, the mean degree of polycondensation is

$$\Pi_c = \frac{W}{N} = 1\Big/\left(1 - \frac{K\,[M_1]}{[H_2O]}\right) \qquad (6.47)$$

This expression is similar to the equation for calculating Π in high-molecular polymerization.

We can also give a generalizing equation for polycondensation by using the concentrations of functional groups. If, for example, the carboxyl and hydroxide groups participate in condensation and the process arrives at equilibrium when the concentrations of these groups, i.e. [—COOH] and [—OH], and also of the formed ester group [—COO—] and water do not change:

$$-COOH + -OH \rightleftharpoons -COO- + H_2O$$

then the expression for the equilibrium constant will be

$$K = \frac{[-COO-]\,[H_2O]}{[-COOH]\,[-OH]}$$

Assume that the initial concentrations of the carboxyl group is $[-COOH]_0$, of the hydroxyl group is $[-OH]_0$, and that the equilibrium degree of conversion of the acid is y. We can now present the equilibrium concentrations in the form:

$$[-COOH] = [-COOH]_0\,(1-y),$$

$$[-OH] = [-COOH]_0 \left(\frac{[-OH]_0}{[-COOH]_0} - y\right)$$

$$[-COO-] = [H_2O] = [-COOH]_0\, y$$

Let us also express the equilibrium constant in terms of y. We obtain

$$K = \frac{y^2}{\{([-OH]_0/[-COOH]_0) - y\}\;(1-y)}$$

But this is the same equilibrium constant as was used above in Eq. (6.47). We can therefore relate the quantities Π_c and y:

$$\Pi_c = \left(1 - \frac{y}{1-y}\right)^{-1}; \quad \frac{[M_1]}{[H_2O]} = \left(\frac{[-OH]_0}{[-COOH]_0} - y\right)\Big/ y$$

If the initial concentrations of the functional groups are the same, namely, $[-COOH]_0 = [-OH]_0$, then the derived equation holds regardless of which of the groups has been denoted by M_1.

If we consider equilibrium for the case when the concentrations of the functional groups are the same and, moreover, the concentration of the water is constant, a similar treatment results in the expressions [44]

$$\Pi_c = \frac{1}{1-y} = \frac{2K/[H_2O]}{\sqrt{1+(4K/[H_2O])} - 1}$$

Hence, when $K/[H_2O] \gg 1$, we have

$$\Pi_c = \sqrt{\frac{K}{[H_2O]}} \tag{6.48}$$

Equation (6.48) is convenient for a qualitative investigation of how the temperature affects the degree of polycondensation. Differen-

tiation of it yields

$$\frac{\partial \ln \Pi_c}{\partial (1/T)} = \frac{1}{2} \frac{\partial \ln K}{\partial (1/T)}$$

But from the equation of an isobar of a chemical reaction

$$\frac{\partial \ln K}{\partial T} = -\frac{\Delta H}{RT^2}$$

we find

$$\frac{\partial \ln \Pi_c}{\partial (1/T)} = -\frac{\Delta H}{R}$$

Consequently,

$$\frac{\partial \ln \Pi_c}{\partial (1/T)} = -\frac{1}{2R} \Delta H \tag{6.49}$$

Since the heat of polycondensation is negative (heat is evolved) a growth in the temperature lowers Π_c, i.e. the molecular mass of the polycondensation product.

It should be noted that if in the course of polycondensation the concentration of the water remains constant (this can be ensured by technological measures), while the concentration of the monomer units entering into the reaction is the same, then the thermodynamic analysis of polycondensation is in essence the same as for polymerization. We can therefore use the methods of determining the equilibrium constants, heats, and changes in the entropy considered above for polymerization. Polycondensation, like polymerization, can be characterized by the limiting temperature.

6.5. Cracking and Pyrolysis

These reactions include chemical transformations of hydrocarbons with the formation of decomposition products. At relatively moderate temperatures (400-600 °C), the molecular products chiefly form by the breaking of one C—C bond (cracking). At elevated temperatures (above 650-700 °C), the number of broken C—C bonds per molecule grows, and C—H bonds are also broken (pyrolysis). From these standpoints, the reactions of cracking and pyrolysis are the opposite of the alkylation and polymerization reactions treated above. The industrial cracking processes are attended by side reactions of carbon and hydrogen redistribution; the thermodynamics of these reactions has also been considered on an earlier page. A special thermodynamic analysis of cracking and pyrolysis reactions allows us to evaluate the heat of a complex process (see Chap. 5) and find the conditions promoting the formation of the decomposition products having a various molecular mass.

The thermodynamics of the molecular reactions of cracking has been developed in the USSR [4, 53]. During recent years, the main achievements in the development of the theory of cracking and

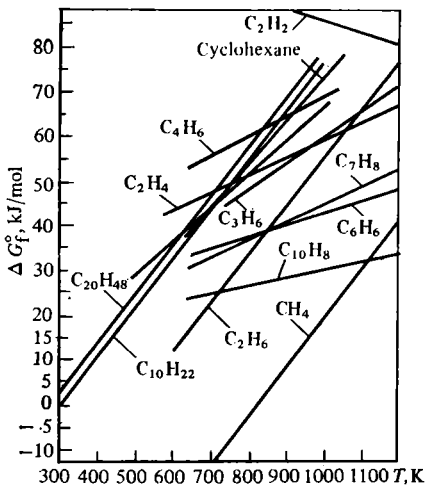


Fig. 30. Temperature dependence of the standard Gibbs energy of formation of hydrocarbons in an ideal gas phase

pyrolysis have been associated with an analysis of the elementary steps of these processes—radical reactions. In this connection, below we consider separately the equilibria of molecular and radical reactions.

6.5.1. Molecular Reactions

Generally the formation of simpler molecules is facilitated by high temperatures and low pressures (the reactions proceed in the gas phase with the absorption of heat and an increase in volume), and the formation of more complex ones, by low temperatures and high pressures.

Naturally, the thermodynamic analysis of decomposition reactions is begun by estimating the probability of decomposition of the hydrocarbons to simple substances or of the reverse reaction—the formation of hydrocarbons from simple substances. The relations to be used for calculations and the values of ΔG_f° are given in Appendices 1 and 2. The effect of the temperature on ΔG_f° for various hydrocarbons is shown in Fig. 30. The values of ΔG_f° are related to one mole of carbon, and the lines have been plotted using approximate expressions presuming a constant heat of a reaction at all temperatures. If $\Delta G^0 > 0$, this only signifies that $K_p^\circ = \exp(-\Delta G^\circ/RT) < 1$, while when $\Delta G^\circ < 0$, we have $K_p > 1$. In both cases, appreciable degrees of conversion are possible. But by comparing ΔG° for various reactions, we can judge on their probability qualitatively, namely, the lower is ΔG°, the higher is the thermodynamic probability.

With this in view, we shall use the data in Fig. 30 for estimating the relative stability of hydrocarbons because the lower a line, the greater is the stability of the relevant hydrocarbon to decomposition into simple substances. Methane can be seen to be the most stable at temperatures up to 1100 K. But even methane can decompose into carbon and hydrogen at moderate temperatures:

Temperature, K	673	873	1073	1173
Content of methane in equilibrium mixture with hydrogen at standard pressure, mole fractions	0.90	0.31	0.06	0.03

More high-molecular normal alkanes such as $C_{10}H_{22}$ can decompose with the same degree of conversion as CH_4 at temperatures lower by 450-500 K. Consequently, the decomposition of $C_{10}H_{22}$ with the formation of methane is thermodynamically probable, but not the opposite case.

Alkanes and cycloalkanes can be seen to be the most stable thermodynamically up to about 700 K. Alkenes are not stable thermodynamically at 300-1200 K, but at low temperatures they can form substantial amounts of the relevant normal alkanes. At high temperatures (for ethane—about 1000 K) and with elevation of the temperature, the probability of conversion of alkanes to alkenes increases. The same holds for aromatics. Moreover, at all temperatures for thermal processes, an increase in the number of their cycles is possible, but not vice versa.

With elevation of the temperature, the stability of dienes grows; they can be produced from other hydrocarbons at high temperatures. The same can be said about acetylene—it can be produced, for example, from ethane at temperatures above 1200 K.

Let us now consider in greater detail data on selected reactions of the mutual transitions of hydrocarbons in cracking and pyrolysis.

Below are given the temperatures (in K) at which the values of ΔG° for a number of reactions become negative [54]:

$C_3H_8 \rightarrow C_2H_4 + CH_4$	>600
$C_4H_{10} \rightarrow C_3H_6 + CH_4$	>600
$C_4H_{10} \rightarrow C_2H_4 + C_2H_6$	>700
$C_6H_{14} \rightarrow C_3H_6 + C_3H_8$	>400
$C_{10}H_{22} \rightarrow C_5H_{10} + C_5H_{12}$	>600
cyclo-$C_5H_{10} \rightarrow C_5H_{10}$	>1000
cyclo-$C_5H_{10} \rightarrow C_2H_4 + C_3H_6$	>800
cyclo-$C_6H_{12} \rightarrow C_6H_{12}$	>900
cyclo-$C_6H_{12} \rightarrow 2C_3H_6$	>700
cyclo-C_6H_{11}—$C_2H_5 \rightarrow 2C_4H_8$	>800
$3C_3H_6 \rightarrow C_4H_6 + 2C_2H_4 + CH_4$	>1100
$C_6H_{12} \rightarrow C_4H_8 + C_2H_4$	>700
$C_6H_{12} \rightarrow 3C_2H_4$	>750
$2C_4H_6 \rightarrow C_6H_5CH{=}CH_2 + 2H_2$	at all temperatures
$2C_4H_6 \rightarrow C_6H_6 + C_2H_4 + H_2$	ditto
$C_4H_6 + C_2H_4 \rightarrow$ *cyclo*-C_6H_{10}	<890
$3C_2H_2 \rightarrow C_6H_6$	<1900
C_6H_5—$C_2H_5 \rightarrow C_6H_6 + C_2H_4$	>850
C_6H_5-*iso*-$C_3H_7 \rightarrow C_6H_6 + C_3H_6$	>700

It should be noted that for reactions of the type $A \rightarrow A_1 + A_2$, the equality of ΔG° to zero signifies that $K_p^\circ = 1$. At standard pressure, a degree of conversion of the feed stock of 71% corresponds to the indicated temperatures. Hence, the reactions will proceed with noticeable degrees of conversion outside of the indicated region, and it becomes obvious that molecular decomposition reactions will be appreciable within a broad temperature interval.

Table 82 presents the possible standard equilibrium constants K_p° and degrees of conversion y (fractions) at standard pressure for selected gas-phase cracking and pyrolysis reactions.

Table 82. **Standard Equilibrium Constants K_p° and Degrees of Conversion y (Fractions) at Standard Pressure for Selected Gas-Phase Cracking and Pyrolysis Reactions**

Reaction	T, K					
	500		700		1000	
	K_p°	y	K_p°	y	K_p°	y
$n\text{-}C_6H_{14} \rightarrow C_2H_4 + n\text{-}C_4H_{10}$	0.004	0.06	2.5	0.84	251	0.99
$n\text{-}C_6H_{12} \rightarrow 2C_3H_6$	0.16	0.37	16	0.97	1585	0.99
$n\text{-}C_6H_{12} \rightarrow 3C_2H_4$	10^{-6}	0	0.2	0.41	3980	0.99
$cyclo\text{-}C_6H_{12} \rightarrow 2C_3H_6$	10^{-5}	0	1.26	0.75	6310	0.99
$cyclo\text{-}C_6H_{12} \rightarrow 3C_2H_4$	10^{-10}	0	0.01	0.10	$10^{4.2}$	0.99

Inspection of the table reveals that for cracking and pyrolysis conditions ($T > 700$ K), the results of a process are determined not by thermodynamic, but by kinetic restrictions.

6.5.2. Radical Reactions

In the theoretical analysis of cracking and pyrolysis processes, the main attention is given to the reactions of formation and transformation of radicals.

Heats of Radical Formation Reactions. Radical formation is a reaction of breaking of the weakest bond A—X in a molecule whose fragments are A and X. The energy of the bond A—X equals the heat of the reaction of formation of the radicals:

$$E_{A-X} = \Delta H_{f,A\cdot} + \Delta H_{f,X\cdot} - \Delta H_{f,AX}$$

There is a certain difference in the values of the mean bond energies given by various authors (for example, [41] and [55]). Below are given the mean bond energies at 298 K for simple molecules of the type of Cl_2, HCl, BrCl, and so on (in kJ/mol):

	I	Br	Cl	F	O	H
H	297	368	431	569	460	435
O	—	—	205	184	146	
F	243	251	255	159		
Cl	209	218	243			
Br	180	192				
I	151					

It is quite obvious that the bonds O—O (peroxide) and I—I (for

example, in an I_2 molecule) will dissociate under thermal action first of all with the formation of radicals.

As regards the bond energies for C—C and C—H, their values also differ according to the data of various authors. For example, the values of the bond energies for CH_3—CH_2 given in [56] vary from 357 to 381 kJ/mol. Moreover, in hydrocarbon molecules, the bond energies depend on the surrounding groups. For example, in a molecule of *n*-octane, the end C—C bonds are stronger, which can be seen from the following values:

$$C\overset{E_1+25}{\text{———}}C\overset{E_1+12}{\text{———}}C\overset{E_1+4}{\text{———}}C\overset{E_1}{\text{———}}C\overset{E_1+4}{\text{———}}C\overset{E_1+12}{\text{———}}C\overset{E_1+25}{\text{———}}C$$

The strength of C—H bonds decreases in the sequence C_{prim}—H > > C_{sec}—H; even the bond C_{sec}—H in the middle of a molecule is somewhat weaker than at an end. Thus, the energies of the C—H bonds in dodecane are as follows:

$$C\overset{E_2+34}{\text{———}}C\overset{E_2+13}{\text{———}}C\overset{E_2+4}{\text{———}}C\overset{E_2}{\text{—}}C\overset{E_2}{\text{—}}C\overset{E_2}{\text{—}}C\overset{E_2}{\text{—}}C\overset{E_2}{\text{—}}C\overset{E_2}{\text{—}}C\overset{E_2+4}{\text{———}}C\overset{E_2+13}{\text{———}}C\overset{E_2+34}{\text{———}}C$$

Table 83 presents the values of the true bond energies given by Magaril [54].

In alkanes and cycloalkanes, the C—H bond is stronger than the C—C one, while in aromatics it is weaker. The conjugation of a C—C bond with an alkene or aromatic nucleus appreciably weakens it.

It should also be noted that the bond energy is redistributed in radicals. Thus, the bond breaking energies in a methane molecule and in radicals are as follows:

Bond	$\dot{C}H_2$—H	$\ddot{C}H$—H	$\dddot{C}$—H	$\dot{C}H_2$—CH_3	$\dot{C}H_2$—C_3H_7	$\dot{C}H_2CH_2$—C_2H_5
E, kJ/mol	362	542	341	310	310	107

The decomposition of radicals along a C—C or C—H bond with the formation of a biradical, for example according to the reactions given above ($\dot{C}H_2$—H→$\ddot{C}H_2$ + H, $\dot{C}H_2CH_3$→$\ddot{C}H_2$ + $\dot{C}H_3$) is difficult in the energy respect in comparison with the decomposition of the radicals with the formation of a molecule and a new radical. The heat of such a decomposition does not equal the energy of the bond in the radical because new bonds form, generally pi bonds in an alkene.

If the reaction $\dot{C}H_2CH_2$—R→$\dot{C}H_2\dot{C}H_2$ + $\dot{R}$ proceeds, its heat equals the energy of the C—C bond in the radical E_{C-C}. But for the complex reaction $\dot{C}H_2CH_2R$→C_2H_4 + R, its heat $\Delta H = E_{C-C} - E_{\pi}$, while for the reaction $\dot{C}H_2CH_2R$→CH_2=CHR +

Table 83. **True Bond Energies [54]**

Bond	E, kJ/mol	Bond	E, kJ/mol
$H-H$	435	$C_6H_5CO-CH_3$	326
CH_3-H	431	$C_3H_7-CH_3$	339
C_2H_5-H	410	$C_4H_9-CH_3$	335
$C_2H_5CH_2-H$	398	$C_2H_5-C_2H_5$	335
n-$C_3H_7CH_2-H$	394	n-C_3H_7-n-C_3H_7	318
$(CH_3)_2CH-H$	394	n-C_4H_9-n-C_3H_7	314
$(C_2H_5)(CH_3)CH-H$	390	n-C_4H_9-n-C_4H_9	310
$(CH_3)_3C-H$	373	$(CH_3)_3C-C(CH_3)_3$	264
$C_6H_5CH_2-H$	348	pi-bond in alkene	239
$CH\equiv C-H$	473	pi-bond in conjugate diene	188
$(C_6H_5)_2C-H$	310	$CH_2=CH-CH_3$	394
$CH_2\equiv CH-H$	435	$CH_2=CHCH_2-CH_3$	260
$CH_2=CHCH_2-H$	322	$CH_2=CH-CH=CH_2$	435
C_6H_5-H	427	$CH_2=CHCH_2-CH_2CH=CH_2$	176
cyclo-$C_6H_{11}-H$	389	$C_6H_5-CH_3$	381
cyclo-C_5H_9-H	389	$C_6H_5-C_2H_5$	368
CH_3-CH_3	360	$C_6H_5CH_2-CH_3$	264
$C_2H_5-CH_3$	348	$C_6H_5-C_3H_7$	360
$C_6H_5CH_2-CH_2C_6H_5$	198	$C_6H_5-C_6H_5$	415
$(C_6H_5)_2CH-CH_2C_6H_5$	159	$C_6H_5CO-C_6H_5$	356
$(C_6H_5)_2CH-CH(C_6H_5)_2$	105	$RCOO-H$	427-469
$(C_6H_5)_3C-C(C_6H_5)_3$	46	CH_3-SH	293
C—C in cyclopropane	201	C_2H_5-SH	289
C—C in cyclobutane	201	$C_6H_5CH_2-SH$	222
C—C in cyclopentane	293	CH_3-SCH_3	301
C—C in cyclohexane	310	$C_2H_5-SC_2H_5$	289
CH_3-OH		$C_6H_5CH_2-SCH_3$	213
$RO-OH$	376	C—H in thiophene	416
$RO-OR$	125-163	C—H in pyridine	429
CH_3CO-CH_3	301		

+ H, we have $\Delta H = E_{C-H} - E_{\pi}$ (where E_{π} is the energy of a pi bond in an alkene). If we assume that $E_{\pi} = 238$ kJ/mol, we shall find that the decomposition of a radical along a 2-bond (β-bond) C—C or C—H is considerably more effective and probable from the energy viewpoint.

Table 84 gives the heats of decomposition of radicals.

Thermodynamic Functions of Radicals. The bond energies can be used to calculate the heats of formation of radicals. The entropies and heat capacities of the radicals are evaluated by the methods of statistical thermodynamics. Calculations performed have been used to develop semi-empirical methods of finding ΔH_f°, S°, and C_p° for radicals. The most widespread of them is Benson's method, which enables one to find the thermodynamic functions of radicals as the sum of the relevant quantities for the groups forming the radicals [57].

Table 84. **Heats of Decomposition of Radicals with the Formation of Alkenes**

Reaction	$\Delta H°$, kJ/mol
$\dot{C}_2H_5 \rightarrow C_2H_4 + \dot{H}$	165
$\dot{C}H_2CH_2CH_3 \rightarrow C_2H_4 + \dot{C}H_3$	115
$\dot{C}H_2CH_2CH_3 \rightarrow C_3H_6 + \dot{H}$	163
$\dot{C}H_2C_7H_{15} \rightarrow C_2H_4 + \dot{C}_6H_{13}$	94
$C-\overset{\overset{C}{\vert}}{C}-\dot{C}-C \rightarrow CH_2=\underset{\underset{CH_3}{\vert}}{C}-CH_3 + \dot{C}_3H_7$	73
$CH=CH\dot{C}H_2 \rightarrow CH_2=C=CH_2 + \dot{H}$	268
$CH_3\dot{C}HC_6H_{13} \rightarrow C_3H_6 + \dot{C}_5H_{11}$	102.5
$C_2H_5\dot{C}HC_5H_{11} \rightarrow C_4H_8 + \dot{C}_4H_9$	113
cyclo-$\dot{C}_6H_{11} \rightarrow$ *cyclo*-$C_6H_{10} + \dot{H}$	151
cyclo-$\dot{C}_6H_{11} \rightarrow H_2C=CHCH_2CH_2CH_2\dot{C}H_2$	75
$CH_2=CH\dot{C}HCH_3 \rightarrow CH_2=CHCH=CH_2 + H$	272
$C_6H_5CH_2\dot{C}H_2 \rightarrow C_2H_4 + \dot{C}_6H_5$	222

A description of Benson's method for molecules is given in Appendix 1.

Here we shall give the thermodynamic functions for the groups forming alkyl radicals (Table 85).

The data of Table 85 can be employed to find the thermodynamic functions of various radicals. For example, the heat of formation of the radical $\dot{C}H_2CH_2CH_3$ can be calculated from the sum of the quantities for the constituent groups: $\dot{C}-(H)_2(C)$, $C-(\dot{C})(C)(H)_2$, and $C-(H)_3(C)$:

$$\Delta H^\circ_{f,298}(C_3H_7) = 149.98 - 20.73 - 42.17 = 87.08 \text{ kJ/mol}$$

The values determined in this way differ from the more accurately determined ones for individual particles by not more than 5 kJ/mol for ΔH°_f and 3 J/(mol·K) for $S°$ and C°_p.

The thermodynamic functions of radicals are given in Table 86.

It is not difficult to calculate the heats and equilibrium constants with the participation of radicals from the thermodynamic functions. As noted by Stepukhovich and Ulitsky, who performed calculations of K°_p for a number of radical reactions [58], such reactions proceed virtually to the end if $\Delta H° < -60$ kJ/mol and do not proceed if $\Delta H° > 60$ kJ/mol.

Table 85. **Thermodynamic Functions of Groups Forming Alkyl Radicals, after Benson***

Radical	$\Delta(\Delta H^\circ_{f,298})$, kJ/mol	ΔS_{298}, J/(mol·K)	ΔC°_p, J/(mol·K)		
			300 K	500 K	1000 K
C—(H)$_3$(C)	−42.17	127.2	25.9	39.33	61.80
C—(H)$_2$(C)$_2$	−20.71	39.41	23.01	34.52	51.63
C—(H)(C)$_3$	−7.95	−50.5	19.0	30.00	42.05
C—(C)$_4$	2.09	−146.86	18.28	30.79	36.65
$\dot{C}$—(H)$_2$(C)	149.98	130.63	25.08	34.71	48.02
$\dot{C}$—(H)(C)$_2$	156.80	44.97	21.60	28.56	37.01
$\dot{C}$—(C)$_3$	154.92	−45.09	17.00	22.69	26.59
C—($\dot{C}$)(C)(H)$_2$	20.73	39.44	23.03	34.54	51.67
C—($\dot{C}$)(C)$_2$(H)	−7.96	−50.54	22.01	31.02	42.08
C—($\dot{C}$)(C)$_3$	6.28	146.96	18.30	30.82	36.68

* When calculating the entropies, take into account the correction for the symmetry of a molecule (see Appendix 1).

Table 86. **Thermodynamic Functions of Radicals**

Radical	$\Delta H^\circ_{f,298}$, kJ/mol	S°_{298}, J/(mol·K)	C°_p, J/(mol·K)		
			300 K	500 K	1000 K
$\dot{H}$	218.14	114.72	20.81	20.81	20.81
$\dot{C}H_3$	142.36	193.02	36.85	44.38	60.71
$\dot{C}_2H_3$	288.90	235.73	40.61	54.84	78.30
$\dot{C}_2H_5$	108.86	250.38	46.47	68.25	107.61
$\dot{C}_3H_5$	169.99	265.46	59.04	83.74	125.61
$\dot{C}H_2C_2H_5$	87.93	286.81	71.60	105.51	159.52
$CH_3\dot{C}HCH_3$	73.69	279.27	71.18	104.26	158.69
$\dot{C}H_2CH_2C_2H_5$	66.32	336.84	97.05	143.15	213.20
$CH_3\dot{C}HC_2H_5$	51.67	339.06	96.47	141.81	212.36
$\dot{C}(CH_3)_3$	28.05	312.35	79.97	127.70	205.16
$\dot{C}H_2CH_2CH_2C_2H_5$	45.60	376.29	120.08	177.70	264.87
$CH_3\dot{C}HCH_2C_2H_5$	30.94	378.50	119.50	176.36	264.03

Table 87. **Heats (in kJ/mol) and Equilibrium Constants of Reactions with the Participation of Radicals**

Reaction	300 K		600 K		900 K	
	$\Delta H°$	$\log K_p^\circ$	$\Delta H°$	$\log K_p^\circ$	$\Delta H°$	$\log K_p^\circ$
Recombination						
$\dot{H}+\dot{C}H_3 \rightarrow CH_4$	−435.45	69.48	−441.52	31.38	−444.60	18.60
$\dot{H}+\dot{C}_2H_5 \rightarrow C_2H_6$	−411.83	64.64	−415.63	28.66	−417.82	16.61
$\dot{C}H_3+\dot{C}H_3 \rightarrow C_2H_6$	−369.54	56.18	−374.25	23.86	−375.36	13.08
$\dot{C}H_3+\dot{C}_2H_5 \rightarrow C_3H_8$	−355.27	52.82	−356.60	21.85	−356.03	11.56
$\dot{C}_2H_5+n\text{-}\dot{C}_3H_7 \rightarrow n\text{-}C_5H_{12}$	−343.50	50.02	−341.77	20.18	−339.21	10.32
$\dot{C}_2H_5+n\text{-}\dot{C}_4H_9 \rightarrow n\text{-}C_6H_{14}$	−342.71	49.34	−341.81	19.54	−339.74	9.68
$n\text{-}C_3H_7+n\text{-}\dot{C}_3H_7 \rightarrow n\text{-}C_6H_{14}$	−343.38	50.17	−342.37	20.31	−339.78	10.45
Disproportionation						
$\dot{H}+\dot{C}_2H_5 \rightarrow H_2+C_2H_4$	−274.71	47.07	−273.35	23.21	−274.23	15.21
$\dot{H}+n\text{-}\dot{C}_3H_7 \rightarrow H_2+C_3H_6$	−285.64	49.56	−285.87	24.69	−287.19	16.35
$\dot{C}H_3+\dot{C}_2H_5 \rightarrow CH_4+C_2H_4$	−273.87	45.75	−274.83	21.88	−275.99	13.92
$\dot{C}H_3+n\text{-}\dot{C}_3H_7 \rightarrow CH_4+C_3H_6$	−284.80	48.24	−287.36	23.37	−288.25	15.06
$\dot{C}_2H_5+\dot{C}_2H_5 \rightarrow C_2H_4+C_2H_6$	−250.26	40.91	−248.93	19.17	−248.51	11.93
$\dot{C}_2H_5+n\text{-}\dot{C}_3H_7 \rightarrow C_2H_6+C_3H_6$	−261.19	43.40	−261.46	20.65	−261.47	13.08
$\dot{C}_2H_5+n\text{-}\dot{C}_4H_9 \rightarrow C_2H_6+C_4H_8$	−260.26	42.65	−261.50	19.96	−262.20	12.37
Hydrogen transition						
$\dot{H}+CH_4 \rightarrow H_2+\dot{C}H_3$	−0.84	1.32	1.48	1.33	1.06	1.23
$\dot{H}+C_2H_6 \rightarrow H_2+\dot{C}_2H_5$	−24.45	6.16	−24.41	4.04	−25.72	3.28
$\dot{H}+C_3H_8 \rightarrow H_2+n\text{-}\dot{C}_3H_7$	−26.17	6.25	−25.18	4.00	−25.33	3.20
$\dot{C}_2H_5+CH_4 \rightarrow C_2H_6+\dot{C}H_3$	23.61	4.84	25.89	−2.71	26.78	−1.98
$n\text{-}\dot{C}_3H_7+CH_4 \rightarrow C_3H_8+\dot{C}H_3$	25.33	−4.92	26.66	−2.68	27.39	−1.91
$n\text{-}\dot{C}_3H_7+C_2H_6 \rightarrow C_3H_8+\dot{C}_2H_5$	1.72	−0.08	0.76	0.04	0.61	0.08
$\dot{C}_2H_3+CH_4 \rightarrow C_2H_4+\dot{C}H_3$	−19.30	2.87	−17.71	1.24	−16.83	0.72
$\dot{C}_3H_5+CH_4 \rightarrow C_3H_6+\dot{C}H_3$	67.75	−11.35	70.00	−5.38	71.58	−3.95
$\dot{C}_2H_3+C_2H_6 \rightarrow C_2H_4+\dot{C}_2H_5$	−42.92	7.71	−43.60	3.95	−43.61	2.70
$\dot{C}_3H_5+C_2H_6 \rightarrow C_2H_6+\dot{C}_2H_5$	44.13	−6.51	44.11	−2.67	44.80	−1.36

Table 87 (*concluded*)

Reaction	300 K		600 K		900 K	
	$\Delta H°$	$\log K_p^\circ$	$\Delta H°$	$\log K_p^\circ$	$\Delta H°$	$\log K_p^\circ$
Decomposition						
$\dot{C}_2H_5 \rightarrow \dot{H} + C_2H_4$	161.58	−23.73	166.69	−9.49	169.31	−4.69
$n\text{-}\dot{C}_3H_7 \rightarrow \dot{H} + C_3H_6$	150.65	−21.24	154.17	−8.01	156.35	−3.54
$n\text{-}\dot{C}_4H_9 \rightarrow \dot{H} + C_4H_8$	151.57	−21.99	154.13	−8.71	155.63	−4.24
$n\text{-}\dot{C}_3H_7 \rightarrow \dot{C}H_3 + C_2H_4$	106.73	−11.99	108.43	−6.65	108.13	0.45
$n\text{-}\dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4$	94.84	−9.54	92.10	−1.38	89.46	1.26
$n\text{-}\dot{C}_5H_{11} \rightarrow n\text{-}\dot{C}_3H_7 + C_2H_4$	94.62	−9.66	92.61	−1.49	89.95	1.14
$sec\text{-}\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6$	111.12	−13.00	111.41	−3.32	110.29	−0.13
$sec\text{-}\dot{C}_5H_{11} \rightarrow \dot{C}_2H_5 + C_3H_6$	98.35	−9.84	95.02	−11.40	92.07	1.34

Heats and Equilibrium Constants of Radical Reactions. The heats and equilibrium constants of radical reactions of recombination ($R_1 + R_2 \rightarrow R_1R_2$), disproportionation ($R_1 + R_2 \rightarrow$ alkane + + alkene), hydrogen transition (substitution, i.e. $R_1 + R_2H \rightarrow$ $\rightarrow R_1H + R_2$), and decomposition ($R \rightarrow$ alkene + $\dot{H}$, $R \rightarrow R_1 +$ + alkene) calculated from the thermodynamic functions of radicals and molecules according to data in [57-59] are presented in Table 87.

Recombination and disproportionation reactions are highly exothermic, therefore when the temperature is elevated their equilibrium constants decrease, but nevertheless remain high: at 900 K they exceed 10^{10}. It should also be noted that if at low temperatures the breaking of a chain is thermodynamically more probable at the expense of a recombination reaction, then at 900 K the probabilities of chain breaking at the expense of recombination and disproportionation are close, while at higher temperatures disproportionation should predominate.

It is also evident that if we consider the decomposition of molecules into radicals, decomposition closer to the middle of a chain will be more probable, while decomposition along a C—H bond is much less probable than along a C—C one.

Using the values of K_p° for a recombination reaction, it is not difficult to calculate the equilibrium concentrations of the radicals that naturally increase with the temperature.

For the reaction of decomposition of a molecule into radicals $R_1R_2 \rightarrow R_1 + R_2$, the equilibrium constant $K_{p,\mathrm{dec}}^\circ$ will be the reciprocal of that for a recombination reaction. If y is the fraction

of decomposed molecules, then for a decomposition reaction we have

$$K_{x,\mathrm{dec}} = \frac{y^2}{1-y^2} = K^{\circ}_{p,\mathrm{dec}} \left(\frac{p^{\circ}}{p}\right)^{-1}$$

For example, for the reaction $\dot{C}_2H_5 + n\text{-}\dot{C}_3H_7 \rightarrow n\text{-}C_5H_{12}$ at 900 K, the value of $K^{\circ}_{p,900} = 10^{10.32}$ (this value is given in Table 87); for 1300 K from the equation of an isobar, we have $K^{\circ}_{p,1300} = 10^{4.20}$. We find that at 900 K and standard pressure, $y^2/(1 - y^2) = 10^{-10.32}$ and $y_{900} \approx 10^{-5}$, i.e. in equilibrium, one molecule from among 10^5 decomposes. For 1300 K, similar calculations yield $y_{1300} \approx 10^{-2}$, and the equilibrium concentration of the radicals will be only two orders of magnitude below the concentration of the molecules. It is noted [58] that such calculations are close to experimental results.

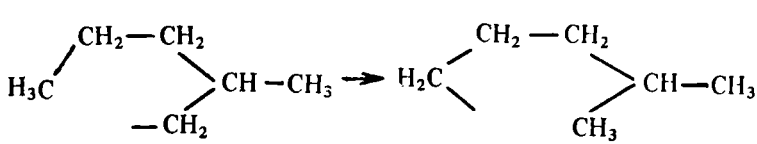
As regards hydrogen transition (substitution) reactions, they are characterized by low heats and, in this connection, by a relatively weak effect of the temperature. It is also significant that at all temperatures the reaction $R_1 + R_2H \rightarrow R_1H + R_2$ as a result of which a more complex radical forms is more probable thermodynamically. For example, the reaction $\dot{H} + CH_4 \rightarrow \dot{C}H_3 + H_2$ is more probable than the reaction $\dot{C}H_3 + H_2 \rightarrow CH_4 + \dot{H}$.

The difference in the behaviour of vinyl ($CH_2{=}\dot{C}H$) and alkenyl ($\dot{C}H_2{-}CH{=}CH_2$) radicals must also be noted, namely, the former can participate in substitution reactions, while the latter cannot.

The probability of endothermic radical decomposition reactions grows substantially with the temperature.

For radicals with three or more carbon atoms, decomposition with the separation of a hydrogen atom and the formation of an alkene ($R \rightarrow H$ + alkene) is less probable than decomposition along a C—C bond, especially along a 2- (β-) one ($R \rightarrow C_2H_4 + R_1$). It is obvious, however, that at high temperatures (above 900 K) the decomposition of radicals (the forward reaction) and their attachment along a pi bond (the reverse reaction) begin to compete.

In explanation of the mechanism of cracking and pyrolysis, the possibility of radical isomerization is presumed. Rice and Kosiakoff, when calculating the yields of lower alkenes from normal alkanes, arrived at the conclusion that account must be taken of the isomerization of radicals with the migration of a hydrogen atom along the carbon chain from the fifth carbon atom to the first one (1,5-regroupings):



(XXII)

Assuming that at 900 K the equilibrium constant of isomerization is close to seven, they obtained good agreement with experimental results.

Later the isomerization of radicals was proved experimentally [59] and is used for calculating the results of pyrolysis [8]; here it is taken into account that in addition to 1,5-transitions, 1,4- and 1,6-transitions are possible, but no others.

Let us estimate the equilibrium constant for the reaction of a 1,5-transition of a primary *n*-alkyl radical.

According to data contained in Table 87, the enthalpy of isomerization at 300 K will be close to —14, and at 1000 K, to —15 kJ/mol (the heat capacities of the radicals are close). The entropy of isomerization is about 2 J/(mol·K) at 300 K and 1 J/(mol·K) at 1000 K. We find the isomerization equilibrium constants to be $K^{\circ}_{p,300} = 335$, $K^{\circ}_{p,900} = 7.4$, and $K^{\circ}_{p,1000} = 6.1$. Thus, Rice's estimate of the equilibrium constant (7 at 873 K) is consistent excellently with thermodynamic data.

Proceeding from the above calculations, we can recommend the following equation for the equilibrium constant of 1,5-isomerization of radicals at temperatures above 600 K:

$$\ln K^{\circ}_{p} = \frac{1805}{T} + 0.24 \qquad (6.50)$$

It can be expected that Eq. (6.50) will also enable us to evaluate the equilibrium constants of other reactions of radical isomerization because the enthalpies and entropies of the reactions will be the same.

In concluding this section, it should be noted that the data on the thermodynamic functions of radicals and their reactions are constantly being refined, and therefore the values given in various sources can differ. For example, for the heat of the reaction $\dot{H} + CH_4 \rightarrow H_2 + \dot{C}H_3$, values differing two times, namely, 4.2 and 8.4 kJ/mol, are given [54], for the heat of the reaction $C_2H_6 \rightarrow 2\dot{C}H_3$, the values ≈358 and ≈375 kJ/mol are given in [58], and so on.

The Use of Thermodynamic Quantities for Estimating the Kinetic Parameters of Radical Reactions. Radical reactions are characterized by true chemical steps; this distinguishes them from reactions of molecules, when a stoichiometric equation is obtained by combining a large number of elementary steps. The kinetic parameters (rate constants, activation energies, preexponential factors) of radical reactions can often be evaluated by using the thermodynamic functions. This enables one to reduce the volume of an experiment when determining these parameters and critically assess the results of the experiment.

The most obvious relations are the one between the enthalpy of a reaction ΔH° and the bond energies of the forward E_{for} and reverse E_{rev} reactions:

$$\Delta H^\circ \approx E_{for} - E_{rev}, \quad \Delta U = E_{for} - E_{rev}$$

and the relation between the equilibrium constant K and the rate constants of the forward k_{for} and reverse k_{rev} reactions:

$$K = \frac{k_{for}}{k_{rev}}$$

In the latter case, the form of the kinetic equation must be taken into account. If the rate of a reaction r is expressed in terms of the molar volume concentrations ($r = k\Pi c_i^{\nu_i}$), then $K = K_c$, while if it is expressed in terms of the partial pressures ($r = k\Pi p_i^{\nu_i}$), then $K = K_p$.

This allows us to find E_{rev} and k_{rev} on the basis of thermodynamic calculations and data on E_{for} and k_{for}. For example, the substitution reaction $CH_4 + \dot{C}_2H_5 \rightarrow \dot{C}H_3 + C_2H_6$ at 900 K is characterized by an enthalpy of $\Delta H^\circ = +27$ kJ/mol and an equilibrium constant of $K_p = K_c = 10^{15}$ (see Table 87).

For the forward reaction, $k_{for} = 10^{8.4}$ m^3/(kmol·s) and $E_{for} = 48$ kJ/mol [58]. We find that for the reverse reaction, $k_{rev} = 10^{15}/10^{8.4} = 10^{6.6}$ m^3/(kmol·s) and $E_{rev} \approx E_{for} - \Delta H^\circ = 48 - 27 = 21$ kJ/mol.

We can find the activation energy of a bimolecular radical reaction $R_1 + R_2H \rightarrow R_1H + R_2$ from the heat of this reaction on the basis of the Polanyi-Semenov correlation equation, which for exothermic reactions has the form

$$E \approx 48.1 + 0.25\Delta H^\circ \quad \text{or} \quad E \approx 48.1 - 0.25\,|\Delta H^\circ|$$

The activation energy of an endothermic (reverse) reaction is greater than that of the exothermic forward reaction by the reaction heat, therefore for endothermic reactions we have

$$E = 48.1 - 0.25\,|\Delta H^\circ| + |\Delta H^\circ| = 48.1 + 0.75\,|\Delta H^\circ| = 48.1 + 0.75\Delta H^\circ$$

In this form of writing the Polanyi-Semenov equation, E and ΔH° are measured in kJ/mol.

A comparison of experimentally found activation energies with the values calculated by the Polanyi-Semenov equation reveals their good agreement (Table 88).

The Polanyi-Semenov equation was derived for bimolecular substitution reactions (hydrogen transition). But this equation was also found to be observed for endothermic reactions of radical decomposition and their reverse exothermic reactions of the attachment of radicals along double (or triple) bonds (Table 89).

Table 88. **Activation Energy of Bimolecular Substitution Reactions**

Reaction	ΔH°_{900}, kJ/mol	Activation energy E, kJ/mol	
		Polanyi-Semenov equation	experiment
$\dot{H}+CH_4 \rightarrow H_2+\dot{C}H_3$	1	48.9	54.0+4.5
$\dot{H}+C_2H_6 \rightarrow H_2+\dot{C}_2H_5$	−26	41.6	40.2+0.4
$\dot{C}H_3+C_2H_6 \rightarrow CH_4+\dot{C}_2H_5$	−27	41.4	45.2
$C_6H_5+CH_4 \rightarrow C_6H_6+\dot{C}H_3$	4.2	51.0	47.0

Table 89. **Activation Energies of Radical Decomposition Reactions**

Reaction	ΔH°_{900}, kJ/mol	Activation energy E, kJ/mol	
		Polanyi-Semenov equation	experiment
$\dot{C}_2H_5 \rightarrow \dot{H}+C_2H_4$	169.3	175	166+4
$n\text{-}\dot{C}_3H_7 \rightarrow \dot{H}+C_3H_6$	156.3	165	140+4
$\dot{H}+C_2H_4 \rightarrow \dot{C}_2H_5$	−169.3	6	7.5+2
$\dot{H}+C_3H_6 \rightarrow n\text{-}\dot{C}_3H_7$	−156.3	9	—
$n\text{-}C_4H_9 \rightarrow \dot{C}_2H_5+C_2H_4$	89.5	115	120-130
$\dot{C}_2H_5+C_2H_4 \rightarrow n\text{-}\dot{C}_4H_9$	−89.5	26	—

Reactions of radical recombination proceed with practically a zero activation energy; consequently, the reverse reactions of radical formation with breaking of a C—C or C—H bond in molecules proceed with an activation energy equal to the energy of breaking the relevant bond.

Thus, when estimating the activation energy, we can use the conditions presented in Table 90.

Hence, thermodynamic calculations allow us to estimate the activation energies of elementary reactions. Knowing the latter, we can, in turn, determine the fractions of a radical reacting in different directions. If a radical can experience transformation in several directions at the rates r_1, r_2, . . ., for example

$$\dot{C}H_2CH_2CH_3 \begin{cases} \xrightarrow{r_1} H+C_3H_6 \\ \xrightarrow{r_2} C_2H_4+\dot{C}H_3 \\ \xrightarrow{r_3} \ddot{C}H_2+\dot{C}_2H_5 \end{cases}$$

Table 90. **Relations for Estimating the Activation Energy of Various Types of Reactions**

Type of reaction	Relation for estimating the activation energy E
$R-H \rightarrow R+\dot{H}$	$E \approx E_{R-H}$
$R_1-R_2 \rightarrow R_1+R_2$	$E \approx E_{R_1-R_2}$
$R_1+\dot{H} \rightarrow R_1-H$	$E \approx 0$
$R_1+R_2 \rightarrow R_1-R_2$	$E \approx 0$
$R_1+R_2 \rightarrow$ alkane + alkene	$E \approx 0$
$R_1+R_2H \rightarrow R_1H+R_2$ $R \rightarrow \dot{H}$ + alkene	$E \approx 48.1-0.25\,\lvert\Delta H^\circ\rvert$
$\dot{H}$ + alkene $\rightarrow R$ Alkene $+ R_1 \rightarrow R$ $R \rightarrow R_1$ + alkene	at $\Delta H^\circ < 0$ $E \approx 48.1+0.75\Delta H^\circ$ at $\Delta H^\circ > 0$

the fraction of the radical participating in the i-th direction is

$$y_i = \frac{r_i}{\sum r_i} = \frac{k_{0,i}\exp(-E_i/RT)}{\sum k_{0,i}\exp(-E_i/RT)}$$

The quantities $k_{0,i}$ for reactions of one type are the same, $k_{0,i} = k_0$, and hence

$$y_i = \frac{\exp(-E_i/RT)}{\sum \exp(-E_i/RT)}$$

Calculations of the relative reactivity of radicals, i.e. of y_i, make it possible to explain the compositions of the molecular products observed in experiments; a large number of examples of such calculations are contained in [54].

Chapter 7

Thermodynamics of Reactions of Hydrocarbons and Their Derivatives with the Evolution or Absorption of Hydrogen

In this chapter, we shall consider reactions proceeding with the evolution of hydrogen (dehydrogenation, cyclization, aromatization) and with its absorption (hydrogenation, hydrogenolysis of C—C, C—S, C—O, and C—N bonds). Some of these reactions can

Table 91. **Relations for Calculating the Equilibrium Degrees of Conversion for Reactions with the Participation of Hydrogen**

Reaction	Relation between K_p°, K_p, and K_x for ideal gas phase	$K_x = f(y)$	$y = f(K_x)$ at $\delta_{A'} = 0$
$A \rightarrow A' + H_2$	$K_x = \frac{K_p}{p} = K_p^\circ \frac{p^\circ}{p}$	$K_x = \frac{(\delta_{A'} + y)(\delta_{H_2} + y)}{(1-y)(1+\delta_{H_2}+\delta_{A'}+y)}$	$y = \frac{1}{2}\left(-\delta_{H_2} + \sqrt{\delta^2_{H_2} + \frac{4K_x(1+\delta_{H_2})}{1+K_x}}\right)$ $y = \sqrt{\frac{K_x}{1+K_x}}$ at $\delta_{H_2} = 0$
$A \rightarrow A' + 2H_2$	$K_x = \frac{K_p}{p^2} = K_p^\circ \left(\frac{p^\circ}{p}\right)^2$	$K_x = \frac{(\delta_{A'} + y)(\delta_{H_2} + 2y)^2}{(1-y)(1+\delta_{H_2}+\delta_{A'}+2y)^2}$	Use Fig. 31a
$A \rightarrow A' + 3H_2$	$K_x = \frac{K_p}{p^3} = K_p^\circ \left(\frac{p^\circ}{p}\right)^3$	$K_x = \frac{(\delta_{A'} + y)(\delta_{H_2} + 3y)^3}{(1-y)(1+\delta_{H_2}+\delta_{A'}+3y)^3}$	Use Fig. 31b
$A \rightarrow A' + 4H_2$	$K_x = \frac{K_p}{p^4} = K_p^\circ \left(\frac{p^\circ}{p}\right)^4$	$K_x = \frac{(\delta_{A'} + y)(\delta_{H_2} + 4y)^4}{(1-y)(1+\delta_{H_2}+\delta_{A'}+4y)^4}$	Use Fig. 31c
$A + H_2 \rightarrow A'$	$K_x = K_p p = K_p^\circ \frac{p}{p_0}$	$K_x = \frac{(\delta_{A'} + y)(1+\delta_{H_2}+\delta_{A'}-y)}{(1-y)(\delta_{H_2}-y)}$	$y = \frac{\delta_{H_2}+1-\sqrt{(\delta_{H_2}+1)^2 - \frac{4K_x\delta_{H_2}}{K_x+1}}}{2}$
$A + 2H_2 \rightarrow A'$	$K_x = K_p p^2 = K_p^\circ \left(\frac{p}{p^\circ}\right)^2$	$K_x = \frac{(\delta_{A'} + y)(1+\delta_{H_2}+\delta_{A'}-2y)^2}{(1-y)(\delta_{H_2}-2y)^2}$	Use Fig. 31d
$A + 3H_2 \rightarrow A'$	$K_x = K_p p^3 = K_p^\circ \left(\frac{p}{p^\circ}\right)^3$	$K_x = \frac{(\delta_{A'} + y)(1+\delta_{H_2}+\delta_{A'}-3y)^3}{(1-y)(\delta_{H_2}-3y)^3}$	Use Fig. 31e
$A + H_2 \rightarrow$ $\rightarrow A_1' + A_2'$	$K_x = K_p = K_p^\circ$	$K_x = \frac{(\delta_{A'} + y)(\delta_{A_2'} + y)}{(1-y)(\delta_{H_2}-y)}$	$y = \frac{K_x(\delta_{H_2}+1) \pm \sqrt{[K_x(\delta_{H_2}+1)]^2 - 4K_x\delta_{H_2}(K_x-1)}}{2(K_x-1)}$

be considered as the forward and reverse steps of a single reversible reaction, namely, hydrogenation-dehydrogenation, cyclization of alkanes into cycloalkanes-hydrogenolysis of cycloalkanes, and so on. For purposes of technology, however, it becomes necessary to establish the conditions favourable for the proceeding of a reaction either only in the forward or only in the reverse direction.

When calculating the heats and equilibrium constants, the reaction can be written in either of the forms

$$\sum \nu_i A_i \xrightarrow[\Delta H_{for}]{K_{for}} \sum \nu_{i'} A_{i'} \text{ or } \sum \nu_{i'} A_{i'} \xrightarrow[\Delta H_{rev}]{K_{rev}} \sum \nu_i A_i$$

because $\Delta H_{for} = -\Delta H_{rev}$, and $K_{for} = 1/K_{rev}$. Therefore, different problems of finding the heats of steps or new equilibrium constants depending on which mixture is the initial one do not arise. However, special calculations have to be performed for finding the degrees of conversion and the equilibrium compositions. Which of the components is the reactant and which is the product are important here. Therefore, below are given relations for calculating the equilibrium degrees of conversion y from the equilibrium constants for typical reactions with the participation of hydrogen (Table 91, see also Fig. 31).

7.1. Reactions with the Participation of Hydrogen in a Non-Ideal Gas Phase

It is not difficult to determine K_x from the thermodynamic functions of substances in the ideal gas phase because $K_p^\circ = \exp(-\Delta G^\circ/RT)$, while K_p° and K_x are related by simple expressions (see Table 91). For a real gas phase

$$K_x = \frac{K_p^\circ}{K_{\gamma^\circ}} \left(\frac{p^\circ}{p}\right)^{\sum \nu_i}$$

and for reactions proceeding at an increased pressure it is necessary to calculate K_{γ°. For hydrogen, $\pi = p/2.1$, $\tau = T/40.2$, $Z_{cr} = 0.29$, and the coefficients $\gamma^\circ(H_2)$ are as follows:

p, MPa	0.01	0.1	1.0	5.0	10.0	20.0	30.0
$\gamma^\circ(H_2)$ at temperatures of:							
300 K	~1.0	1.0	1.0	1.0	1.06	1.13	1.20
500 K	1.0	1.0	1.0	1.0	1.04	1.08	1.12
800 K	1.0	1.0	1.0	1.0	1.03	1.05	1.08

The deviations of $\gamma^\circ(H_2)$ from unity must be taken into consideration only at pressures above 10 MPa. The fugacity coefficients of hydrocarbons change to a greater degree. Table 92 compares the fugacity coefficients at two temperatures of a normal alkane, 1-*n*-alkene, and an aromatic with the same number of carbon atoms because K_{γ° includes the ratios of γ° of the hydrocarbons.

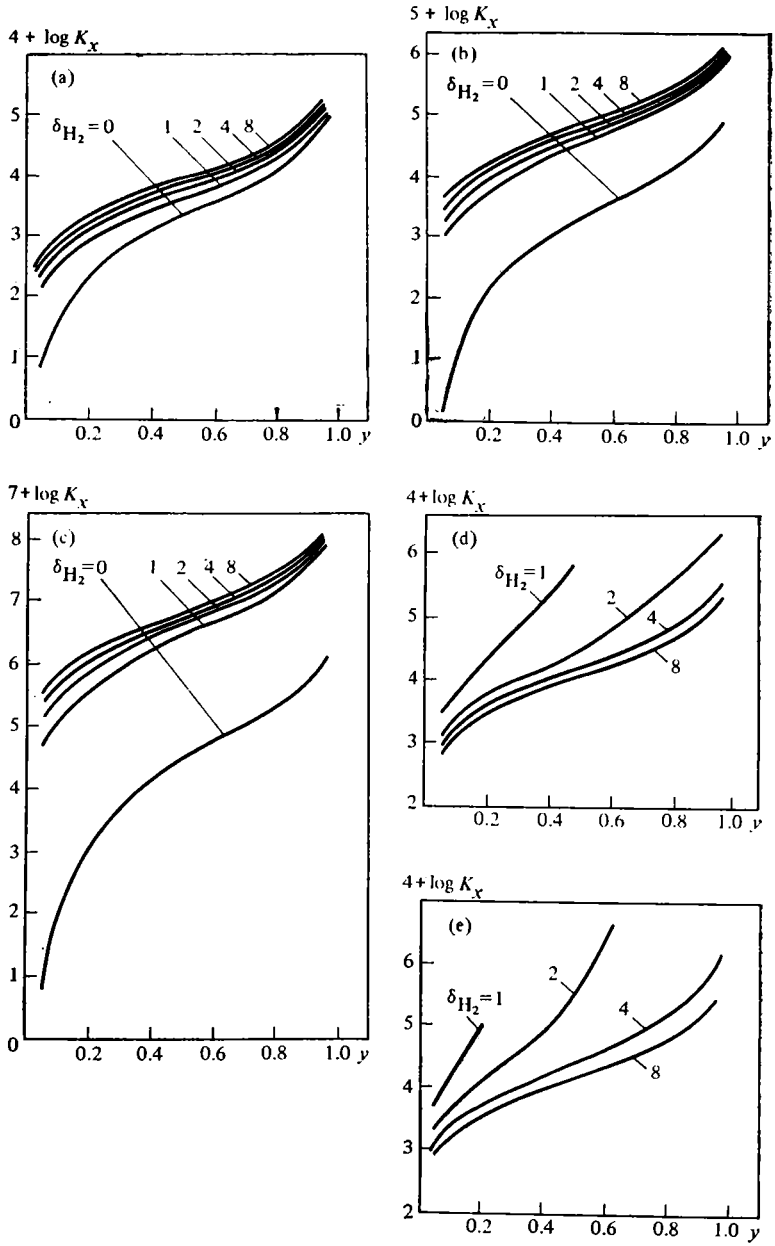


Fig. 31. Relation between the equilibrium constants K_x and the equilibrium degrees of conversion y for reactions of hydrocarbons with the evolution or absorption of hydrogen for various molar ratios δ_{H_2} of the hydrogen and feed stock (the numbers on the curves). The reaction types are:

a—$A \rightarrow A' + 2H_2$; *b*—$A \rightarrow A' + 3H_2$; *c*—$A \rightarrow A' + 4H_2$; *d*—$A + 2H_2 \rightarrow A'$; *e*—$A + 3H_2 \rightarrow A'$

Table 92. **Fugacity Coefficients at 500 and 800 K and Various Pressures of an *n*-Alkane, 1-*n*-Alkene, and Aromatic with the Same Number of Carbon Atoms**

Pressure	$\gamma^\circ_{n\text{-alkane}}/\gamma^\circ_{1\text{-}n\text{-alkene}}$		$\gamma^\circ_{n\text{-alkane}}/\gamma^\circ_{\text{arom.}}$		$\gamma^\circ_{1\text{-}n\text{ alkene}}/\gamma^\circ_{\text{arom.}}$	
	500 K	800 K	500 K	800 K	500 K	800 K
up to 0.1	1.0	1.0	1.0	1.0	1.0	1.0
1.0	1.02	1.05	0.95	0.96	0.93	0.90
5.0	1.0	1.05	0.90	0.94	0.90	0.89
10.0	1.0	1.02	0.65	1.0	0.65	0.98
20.0	1.0	1.0	0.80	1.1	0.80	1.1
30.0	1.0	1.0	1.0	1.3	1.0	1.3

At pressures below 1.0 MPa and above 20 MPa, and at temperatures above 800 K, the ratio $\gamma^\circ_i/\gamma^\circ_j$ differs only slightly from unity. Inspection of Table 92 reveals that up to 5 MPa we have $\gamma^\circ(H_2) \approx 1$ and, consequently, we can be guided by the following recommendations when calculating K_{γ°:

p, MPa	$T = 300$ K	$T > 500$ K
Up to 1.0	$K_{\gamma^\circ} = \gamma^\circ_{A'}/\gamma^\circ_A$	$K_{\gamma^\circ} = 1$
1.0 to 5.0	Ditto	$K_{\gamma^\circ} = \gamma^\circ_{A'}/\gamma^\circ_A$
Above 5.0	Ditto	$K_{\gamma^\circ} = \gamma^\circ_{A'}(\gamma^\circ_{H_2})^{\nu_{H_2}}/\gamma^\circ_A$

Here A is the reactant hydrocarbon, A′ is the product, $\nu(H_2)$ is positive if H_2 is a product and negative if H_2 is a reactant; the error of the approximations does not exceed 10%.

Effect of the Hydrogen: Feed Stock Ratio on the Equilibrium Degrees of Conversion. The equilibrium degrees of conversion of reactions with the participation of hydrogen are greatly affected not only by the temperature and pressure (they determine the quantity K_x), but also by the molar ratio of the hydrogen and feed stock $\delta(H_2)$. The latter, as can be seen from the data of Table 91, can substantially change the equilibrium degree of conversion y at constant temperature and pressure. Since industrial processes of both hydrogenation and dehydrogenation are conducted by feeding hydrogen into the reaction zone (for example, to maintain a stable activity of the catalyst), we shall illustrate the effect of $\delta(H_2)$ on y using specific examples for hydrogenation and dehydrogenation. Assume that the hydrogenation reaction $A + H_2 \rightarrow A'$ is proceeding. Hence, depending on $\delta(H_2)$ and K_x, we obtain the following equilibrium degrees of conversion y:

	$K_x = 1$				$K_x = 2$			
$\delta(H_2)$	0	1	2	5	10	0	1	2	5
y, fractions	0	0.29	0.38	0.45	0.48	0	0.50	0.63	0.71

In both cases, by increasing $\delta(H_2)$, one can increase the degree of conversion by about 20%.

The effect of $\delta(H_2)$ is just as noticeable in dehydrogenation. Thus, for the reaction $A \rightarrow A' + H_2$, we obtain:

	$K_x = 1$			$K_x = 2$		
$\delta(H_2)$	0	1	5	0	1	5
y, fractions	0.71	0.61	0.54	0.82	0.76	0.70

A growth in $\delta(H_2)$ results in a reduction in the degree of conversion and its effect is stronger, the lower is the equilibrium constant.

Reactions with the Participation of Hydrogen in a Gas-Liquid System. A number of reactions with gaseous hydrogen, chiefly hydrogenation, are conducted at moderate temperatures when the reactants and (or) the products are in the liquid phase. If for the same temperature thermodynamic calculations have been performed for a gas-phase reaction (all the components are gaseous), i.e. ΔH°, K_p°, and the equilibrium composition have been found, one can go over to the thermodynamic characteristics of equilibrium in a gas-liquid system. For an ideal solution, $p_i = p_i^\circ x_i$ (where p_i° is the saturated vapour pressure of component i, and x_i is the mole fraction of component i in the liquid). Consequently, disregarding the content of H_2 in the liquid phase [$x(H_2)$ is small], we have for the vapour (v) phase:

$$x_A^v = \frac{p_A}{p_A + p_{A'} + p(H_2)} = \frac{p_A^\circ x_A}{p_A^\circ x_A + p_{A'}^\circ x_{A'} + p(H_2)}$$

$$x_{A'}^v = \frac{p_{A'}}{p_A + p_{A'} + p(H_2)} = \frac{p_{A'}^\circ x_{A'}}{p_A^\circ x_A + p_{A'}^\circ x_{A'} + p(H_2)}$$

If the liquid phase contains only A and A′, i.e. $x_A + x_{A'} \approx 1$, then

$$x_A^v = \frac{p_A^\circ x_A}{p_A^\circ x_A + p_{A'}^\circ (1 - x_A) + p(H_2)}$$

or

$$x_A = [p(H_2) + p_{A'}^\circ] \Big/ \left[p_{A'}^\circ + \left(\frac{1}{x_A^v} - 1 \right) p_A^\circ \right] \qquad (7.1)$$

By using Eq. (7.1), we can easily find x_A^v, i.e. the content of A in the liquid phase, from the mole fraction x_A^v of A in the gas phase and the saturated vapour pressures of the components p_i°.

It should be noted, however, that in the overwhelming majority of real situations there are no problems in calculating the equilibrium composition of gas-liquid reactions because at moderate temperatures hydrogenation proceeds practically to the end (see Ta-

ble 93), i.e. $x_A^v \approx 0$ (the reactant is consumed completely in the gas-phase reaction) and, consequently, $x_A^v \approx 0$ (the reactant is completely consumed in the gas-liquid reaction). To go over from the heat of a gas phase reaction ΔH° to that of a gas-liquid reaction $\Delta H^\circ_{g,lq}$, we can use the heats of vaporization of A and A′, namely, $\Delta H^\circ_{v,A}$ and $\Delta H^\circ_{v,A'}$:

$$\Delta H^\circ_{g,lq} = \Delta H^\circ + \Delta H^\circ_{v,A} - \Delta H^\circ_{v,A'}$$

(the exact calculation of ΔH should take into account the effect of the pressure on ΔH_v, but ΔH° and ΔH differ only slightly). Since the difference $\Delta H^\circ_{v,A} - \Delta H^\circ_{v,A'}$ is small, for example, in the hydrogenation of benzene to cyclohexane this difference is less than 0.1 kJ/mol, we can consider that $\Delta H^\circ_{g,lq} \approx \Delta H^\circ$. These simplifications result in the standard Gibbs energies ΔG° of the gas-phase and $\Delta G_{g,lq}$ of the gas-liquid reactions being close:

$$\Delta G^\circ_{g,lq} \approx \Delta G^\circ$$

Naturally, $\Delta G^\circ_{g,lq}$ and $\Delta H^\circ_{g,lq}$ can also be calculated from the standard thermodynamic functions of A and A′ for the liquid state. It should be had in view that the value of $\Delta G^\circ_{g,lq}$ can be used to find the constant $K^\circ_{f,a}$, and for an ideal solution $-K^\circ_{p,x}$. This treatment is aimed at showing that for most gas-liquid reactions of hydrogenation we can use quantities found from the properties of substances in the state of an ideal gas.

Special calculations described in Sec. 2.6 may be needed for reactions attended by the hydrogenolysis of C—C, C—S, C—N, and C—O bonds.

7.2. Hydrocarbon Hydrogenation (Dehydrogenation), Cyclization (Decyclization), and Hydrocracking Reactions

To estimate ΔH° and K°_p for these reactions, we can use the generalized relations $\Delta H^\circ = \Delta H^\circ (T, n)$ and $K^\circ_p = K^\circ_p (T, n)$, where n is the number of carbon atoms for various hydrocarbons, that are given in Appendix 1.

1. Hydrogenation reaction:

$$1\text{-}n\text{-alkene} + H_2 \rightarrow n\text{-alkane}$$

(there are four or more carbon atoms in a molecule). Since $\Delta H^\circ_1 = \Delta H^\circ_{f,alkane} - \Delta H^\circ_{f,alkene}$, and $\log K^\circ_{p,1} = \log K^\circ_{p,f,alkane} - \log K^\circ_{p,f,alkene}$, we find

$$\Delta H^\circ_1 = (-119 + 0.21n) - (25.30 + 1.87n)\,10^{-3}T + (0.72 + 0.48n)\,10^{-5}T^2 + (0.19 - 0.22n)\,10^{-8}T^3, \text{ kJ}$$

$$\log K^\circ_{p,1} = -(4.86 + 0.20n) - (2.58 - 0.24n)\,10^{-3}T + (0.09 - 0.01n)\,10^{-5}T^2 + (6.36 + 0.02n)\,10^3/T$$

Table 93. **Heats $\Delta H°$ (in kJ) and Equilibrium Constants K_p° for Reactions**

Hydrogenation reaction	Temperature, K		
	300		500
	$\Delta H°$	K_p°	$\Delta H°$
Acetylene:			
$C_2H_2 + H_2 \rightarrow C_2H_4$	—174.6	3.4×10^{24}	—179.7
1-*n*-Alkenes:			
$C_2H_4 + H_2 \rightarrow C_2H_6$	—137.1	3.5×10^{17}	—140.6
$C_3H_6 + H_2 \rightarrow C_3H_8$	—124.3	9.3×10^{14}	—127.3
$C_4H_8 + H_2 \rightarrow C_4H_{10}$	—126.1	2.3×10^{15}	—129.0
$C_{10}H_{20} + H_2 \rightarrow C_{10}H_{22}$	—125.6	1.8×10^{15}	—128.6
Conjugate dienes to 1-*n*-alkenes:			
$C_4H_6 + H_2 \rightarrow C_4H_8$	—110.4	6.1×10^{13}	—114.7
$C_5H_8 + H_2 \rightarrow C_5H_{10}$	—126.5	6.7×10^{15}	—130.8
Aromatics to six-membered cycloalkanes:			
$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$	—206.1	8.5×10^{16}	—216.1
$C_6H_5-CH_3 + 3H_2 \rightarrow C_6H_{11}-CH_3$	—205.0	2.7×10^{16}	—213.2
$C_6H_4(CH_3)_2 + 3H_2 \rightarrow C_6H_{10}(CH_3)_2$	—194.8	2.3×10^{14}	—202.7
Alkenyl-aromatics to alkyl-aromatics:			
$C_6H_5-CH=CH_2 + H_2 \rightarrow C_6H_5-C_2H_5$	—117.7	2.8×10^{14}	—121.5
$C_6H_5C(CH_3)=CH_2 + H_2 \rightarrow C_6H_5CH(CH_3)_2$	—109.1	2.6×10^{12}	—112.4

of Hydrocarbons with the Participation of Hydrogen in the Ideal Gas Phase

Temperature, K			Approximate dependence of K_p° on T for temperature interval 300-800 K
500	800		
K_p°	ΔH°	K_p°	
1.6×10^{12}	—183.6	1.3×10^{5}	$K_p^\circ = \exp(-15.35+21\,550/T)$
8.0×10^{7}	—143.6	220	$K_p^\circ = \exp(-15.80+16\,880/T)$
1.6×10^{6}	—129.3	15.6	$K_p^\circ = \exp(-16.42+15\,410/T)$
3.1×10^{6}	—130.9	25.2	$K_p^\circ = \exp(-16.19+14\,090/T)$
3.0×10^{6}	—130.6	23.5	$K_p^\circ = \exp(-16.27+15\,425/T)$
9.4×10^{5}	—118.9	25.3	$K_p^\circ = \exp(-14.21+13\,790/T)$
7.9×10^{6}	—134.4	49.4	$K_p^\circ = \exp(-15.87+15\,700/T)$
1.8×10^{2}	—220.6	5×10^{-7}	$K_p^\circ = \exp(-46.87+25\,760/T)$
76	—215.6	3×10^{-7}	$K_p^\circ = \exp(-46.83+25\,400/T)$
3.4	—204.2	3×10^{-8}	$K_p^\circ = \exp(-42.27+21\,106/T)$
1.4×10^{6}	—124.4	21.2	$K_p^\circ = \exp(-15.21+14\,570/T)$
5.2×10^{4}	—114.0	1.9	$K_p^\circ = \exp(-16.20+13\,440/T)$

2. Hydrogenation reaction:

$$1\text{-}n\text{-alkyne} + 2H_2 \rightarrow n\text{-alkane}$$

(there are four or more carbon atoms in a molecule). Since $\Delta H_2^\circ = \Delta H_{f,\text{alkane}}^\circ - \Delta H_{f,\text{alkyne}}^\circ$, and $\log K_{p,2}^\circ = \log K_{p,f,\text{alkane}}^\circ - \log K_{p,f,\text{alkyne}}^\circ$, we find

$$\Delta H_2^\circ = -(275.0 - 0.23n) - (65.0 + 2.1n)\,10^{-3}T + (3.71 + 0.50n)\,10^{-5}T^2 - (0.51 + 0.23n)\,10^{-8}T^3 \text{ kJ}$$

$$\log K_{p,2}^\circ = -(10.09 + 0.34n) - (4.40 - 0.41n)\,10^{-3}T + (0.16 - 0.02n)\,10^{-5}T^2 + (14.89 + 0.05n)\,10^3/T$$

3. Hydrogenation reaction:

$$\text{aromatic (arom.)} + 4H_2 \rightarrow n\text{-alkane}$$

(there are six or more carbon atoms in a molecule). This reaction is the reverse one with respect to the reaction of aromatization of n-alkanes. Since $\Delta H_3^\circ = \Delta H_{f,\text{alkane}}^\circ - \Delta H_{f,\text{arom.}}^\circ$, and $\log K_{p,3}^\circ = \log K_{p,f,\text{alkane}}^\circ - \log K_{p,f,\text{arom.}}^\circ$, we obtain

$$\Delta H_3^\circ = -(201.71 + 2.96n) + (-166.32 + 14.05n)\,10^{-3}T + (15.39 - 1.54n)\,10^{-5}T^2 + (-4.48 + 0.51n)\,10^{-8}T^3 \text{ kJ}$$

$$\log K_{p,3}^\circ = (-20.0 + 0.16n) + (12.66 - 0.10n)\,10^3/T + (-5.16 + 0.06n)\,10^{-3}T + (0.28 - 0.02n)\,10^{-5}T^2$$

4. Hydrogenation reaction:

$$\text{five-membered cycloalkane } (CA_5) + H_2 \rightarrow \text{alkane}$$

(there are six or more carbon atoms in a molecule). This reaction is the reverse one with respect to the cyclization of an alkane and is an example of the hydrogenolysis of a C—C bond in a five-membered ring. Since $\Delta H_4^\circ = \Delta H_{f,\text{alkane}}^\circ - \Delta H_{f,CA_5}^\circ$ and $\log K_{p,4}^\circ = \log K_{p,f,\text{alkane}}^\circ - \log K_{p,f,CA_5}^\circ$, we find

$$\Delta H_4^\circ = -(43.70 + 3.57n) - (70.97 - 14.81n)\,10^{-3}T + (7.46 - 1.52n)\,10^{-5}T^2 - (2.52 - 0.47n)\,10^{-8}T^3 \text{ kJ}$$

$$\log K_{p,4}^\circ = -(66.16 - 8.58n) + (15.95 - 1.78n)\,10^3/T + (82.32 - 11.36n)\,10^{-3}T - (3.13 - 0.46n)\,10^{-5}T^2$$

5. Hydrogenation reaction:

$$\text{six-membered cycloalkane } (CA_6) + H_2 \rightarrow \text{alkane}$$

(there are six or more carbon atoms in a molecule). This reaction is the reverse one with respect to the cyclization of an alkane and is an example of the hydrogenolysis of a C—C bond in a six-mem-

bered ring. Using the relations for ΔH_f° and $\log K_{p,f}^\circ$ we find

$$\Delta H_5^\circ = -(21.09 + 3.09n) - (0.68 - 6.12n)\,10^{-3}T - (1.0 + 0.64n)\,10^{-5}T^2 + (0.12 + 0.24n)\,10^{-8}T^3 \text{ kJ}$$

$$\log K_{p,5}^\circ = -(41.52 - 3.64n) + (12.0 - 1.05n)\,10^3/T + (3.42 - 1.80n)\,10^{-3}T + (-0.35 + 0.10n)\,10^{-5}T^2$$

6. Reaction of hydrocracking of alkanes:

$$\text{alkane}_n + H_2 \rightarrow \text{alkane}_m + \text{alkane}_{n-m}$$

(there are at least four carbon atoms in the low-molecular molecule).

The thermodynamic characteristics of this reaction vary insignificantly depending on the degree of isomerization of the products. In real processes, hydrocracking yields larger amounts of isoalkanes than of normal ones. For approximate estimates according to the data on ΔH_f° and $\log K_{p,f}^\circ$ we find

$$\Delta H_6^\circ = -19.55 - 95.18 \times 10^{-3}T + 8.12 \times 10^{-5}T^2 - 2.53 \times 10^{-8}T^3 \text{ kJ}$$

$$\log K_{p,6}^\circ = 1.67 + 2.45 \times 10^3/T - 3.14 \times 10^{-3}T + 0.196 \times 10^{-5}T^2$$

The expressions for ΔH° and $\log K_p^\circ$ given for the above six independent reactions can be used to find the relevant quantities for a number of other reactions depending on them. Thus, the reaction of hydrogenation of aromatics to six-membered cycloalkanes: Arom. $+ 3H_2 \rightarrow CA_6$ (reaction No. 7) can be obtained as the difference between reactions No. 5 ($CA_6 + H_2 \rightarrow$ alkane) and No. 3 (Arom. $+ 4H_2 \rightarrow$ alkane), namely, (7) = (3) — (5). Hence, $\Delta H_7^\circ = \Delta H_3^\circ - \Delta H_5^\circ$ and $\log K_{p,7}^\circ = \log K_{p,3}^\circ - \log K_{p,5}^\circ$.

The heats and equilibrium constants for exothermic hydrogenation reactions are presented in Table 93.

A glance at Table 93 reveals that the hydrogenation of acetylene and ethylene can be performed even at 800 K: at $K_x = 200$, $p = p^\circ$, and $\delta(H_2) = 1$ the equilibrium degree of conversion is 93% and it will be still higher at $\delta(H_2) > 1$. The hydrogenation of alkenes with three or more carbon atoms, dienes, and alkenylbenzenes at 800 K is limited thermodynamically: at $p = p^\circ$, $\delta(H_2) = 1$, and equilibrium constants K_x from 15 to 50, it is possible to hydrogenate from 75 to 86% of the feed stock, while for 1-methylstyrene ($K_x = 1.9$)— only 19%.

The hydrogenation of aromatics at elevated temperatures causes the greatest thermodynamic difficulties. At 800 K, it does not practically proceed, and even at 500 K [$p = p^\circ$, $\delta(H_2) = 3$] only about 85% of benzene, 80% of toluene, and 45% of *p*-xylene are involved in the reaction.

It is evident that the extent of hydrogenation reactions grows with lowering of the temperature, an increase in the pressure, and dilution with hydrogen.

As regards the reverse reactions of dehydrogenation, they will be favoured by high temperatures, low pressures, and dilution with hydrogen. We have already noted that at 800 K and $p = p^\circ$ ethylene can be hydrogenated with a degree of conversion exceeding 93%. But at the same temperature and pressure, the reverse reaction of ethane dehydrogenation is possible: $K'_x = 1/K_x = 4.5 \times 10^{-3}$. If $\delta(H_2) = 0$, the degree of conversion of ethane can reach 6.7%. The use of vacuum, for example, $p = 0.3p^\circ$, makes it possible to increase this degree up to about 12%.

Table 94. **Temperature (in °C) at Which the Equilibrium Degree of Conversion is Reached for the Dehydrogenation of *n*-Alkanes**

Equilibrium degree of conversion, y, %	Number of carbon atoms in *n*-alkane				
	2	3	4*	5*	6*
5	500	410	375-415	360-405	≈335
10	555	455	420-460	410-450	≈380
20	615	510	470-515	440-505	≈425
30	660	540	505-555	465-535	≈445
40	695	570	530-590	490-560	≈470
50	725	595	555-625	520-585	≈495
60	755	625	580-660	545-615	≈520
70	790	660	610-700	575-650	≈550
80	830	700	645-740	605-685	≈585
90	900	750	700-800	650-730	≈625
95	960	815	745-860	695-790	≈670

* Temperature interval for producing various *n*-alkenes.

Table 94 gives approximate data [4] on the temperature at which the equilibrium degree of conversion is reached for the dehydrogenation of various *n*-alkane hydrocarbons to alkenes at atmospheric pressure and $\delta(H_2) = 0$.

Table 95 contains similar data for reactions of preparation of dienes [4].

The heats and equilibrium constants for the cyclization of alkanes and alkenes to aromatics and cycloalkanes are given in Table 96.

Examination of the data in Table 96 shows that the cyclization of alkanes to aromatics and all kinds of cyclization of alkanes are

Table 95. **Temperature (in °C) at Which the Equilibrium Degree of Conversion Is Reached for Reactions of Production of Dienes**

Reaction	Pressure, MPa	Equilibrium degree of conversion y, %						
		5	10	20	50	70	90	95
n-Butane →	0.1	500	540	585	660	700	740	775
→ 1,3-butadiene	0.01	420	440	475	545	585	620	630
1-*n*-Butene →	0.1	435	485	550	665	730	855	925
→ 1,3-butadiene	0.01	370	405	445	540	600	675	725
cis-2-Butene → → 1,3-butadiene	0.1	430	480	540	635	695	805	855
1-Pentene → *cis*- and *trans*-1,3-pentadienes	0.1	335	380	430	525	590	680	750
2-Methyl-1-butene → → isoprene	0.1	430	480	545	650	715	830	899

thermodynamically probable at elevated (above 600 K) temperatures ($\Delta H^\circ > 0$). An aromatic is the thermodynamically most probable cyclization product. The cyclization of alkenes to cycloalkanes is exothermic. Although it is favoured by low temperatures, considerable degrees of conversion are possible even at 1000 K. This reaction is sometimes considered as a step in alkane cyclization.

Let us consider the dehydrogenation of ethylbenzene as an example of thermodynamic analysis. The reaction of styrene hydrogenation is discussed in [26], where the reliability and satisfactory agreement of the data obtained by different authors is shown. The values of ΔH° and K_p° are given in Table 93. They are consistent with the data given by Stull [26].

In accordance with the data in the present chapter, at moderate pressures $K_{\gamma^\circ} = 1$, and this substantiates the calculations for ideal systems given in [26]. Figures 32-34 show how ΔH° and the equilibrium composition depend on the temperature and pressure. Stull [26] has failed to discuss the effect of the quantity $\delta(H_2)$, which is very important for industrial analysis, on the equilibrium composition.

Below is shown the effect of $\delta(H_2)$ on the equilibrium degrees of conversion of ethylbenzene at various values of the equilibrium constant and at standard pressure:

K_p°	0.05	2.0	21.3
$\delta(H_2)$	0	0.5	1.0
y at temperatures:			
800 K	0.22	0.12	0.09
1000 K	0.82	0.78	0.76
1200 K	0.98	0.975	0.97

Table 96. **Heats $\Delta H°$ (in kJ) and Equilibrium Constants K_p° of Alkane and Alkene Cyclization Reactions**

Cyclization reaction	Temperature, K											
	300		400		500		600		800		1000	
	$\Delta H°$	K_p°	$\Delta H°$	K_p°	$\Delta H°$	K_p°	$\Delta H°$	K_p°	$\Delta H°$	K_p°	$\Delta H°$	K_p°
Alkanes to aromatics:												
n-hexane → benzene + $4H_2$	250.2	$10^{-22.5}$	255.3	$10^{-11.5}$	259.5	$10^{-4.8}$	262.8	0.631	266.8	$10^{5.5}$	268.1	$10^{9.0}$
n-heptane → toluene + $4H_2$	237.9	$10^{-19.7}$	242.8	$10^{-9.3}$	247.0	0.001	250.3	31.6	254.6	$10^{7.0}$	256.4	$10^{10.3}$
n-octane → o-xylene + $4H_2$	227.6	$10^{-18.3}$	233.0	$10^{-8.3}$	237.2	0.008	240.3	100	244.0	$10^{7.3}$	244.8	$10^{10.5}$
n-octane → m-xylene + $4H_2$	225.8	$10^{-17.7}$	230.7	$10^{-7.8}$	234.6	0.183	237.5	251.2	240.8	$10^{7.6}$	241.5	$10^{10.8}$
n-octane → p-xylene + $4H_2$	226.5	$10^{-18.1}$	231.3	$10^{-8.1}$	235.1	0.008	237.8	125.9	240.9	$10^{7.3}$	241.3	$10^{10.4}$
n-octane → ethylbenzene + $4H_2$	238.4	$10^{-19.7}$	243.5	$10^{-9.3}$	247.7	0.001	251.0	31.6	255.1	$10^{7.0}$	256.2	$10^{10.3}$
n-nonane → n-propylbenzene + $4H_2$	236.9	$10^{-19.4}$	242.2	$10^{-9.0}$	246.4	0.003	249.8	50.1	253.9	$10^{7.2}$	255.1	$10^{10.5}$
n-decane → n-butylbenzene + $4H_2$	236.0	$10^{-19.3}$	241.1	$10^{-8.9}$	245.5	0.003	248.8	63.1	252.9	$10^{7.2}$	254.1	$10^{10.5}$
2-methylhexane → toluene + $4H_2$	245.1	$10^{-20.6}$	250.0	$10^{-9.8}$	254.1	$10^{-3.2}$	257.4	15.8	261.8	$10^{6.9}$	263.5	$10^{10.3}$
2-methylheptane → ethylbenzene + $4H_2$	245.4	$10^{-20.4}$	250.5	$10^{-9.6}$	254.8	0.0001	258.0	31.6	262.1	$10^{7.1}$	263.3	$10^{10.6}$
Alkenes to aromatics:												
1-hexene → benzene + $3H_2$	124.6	$10^{-7.3}$	128.1	0.016	131.0	39.8	133.3	$10^{3.9}$	136.3	$10^{6.8}$	137.3	$10^{8.6}$
2-hexene → benzene + $3H_2$	135.4	$10^{-9.2}$	139.4	$10^{-3.2}$	142.8	2.5	145.6	1000	149.2	$10^{6.2}$	150.6	$10^{8.1}$
3-hexene → benzene + $3H_2$	130.6	$10^{-8.0}$	134.8	0.005	138.2	20.0	141.0	$10^{3.7}$	144.4	$10^{6.8}$	145.8	$10^{8.7}$
1-heptene → toluene + $3H_2$	112.4	$10^{-4.5}$	115.7	3.2	118.5	$10^{3.5}$	120.9	$10^{5.6}$	124.1	$10^{8.3}$	125.7	$10^{9.9}$
1-octene → ethylbenzene + $3H_2$	112.8	$10^{-4.5}$	116.3	3.2	119.2	$10^{3.6}$	121.6	$10^{5.7}$	124.6	$10^{8.3}$	125.5	$10^{10.0}$

1-nonene → n-propylbenzene − $3H_2$	111.4	$10^{-4.2}$	115.0	5.0	118.0	$10^{3.8}$	120.4	$10^{5.8}$	123.3	$10^{8.5}$	124.4	$10^{10.1}$
1-decene → *n*-butylbenzene + $3H_2$	110.4	$10^{-4.0}$	113.9	7.9	116.9	$10^{3.9}$	119.3	$10^{5.9}$	122.3	$10^{8.6}$	123.4	$10^{10.2}$
Alkanes to five-membered cycloalkanes:												
n-pentane → cyclopentane + H_2	69.2	$10^{8.2}$	68.5	$10^{-5.2}$	68.2	$10^{-3.4}$	68.1	0.006	68.2	0.200	68.6	1.6
n-hexane → methylcyclopentane + H_2	60.5	$10^{-6.2}$	60.2	$10^{-3.6}$	60.2	0.010	60.3	0.100	60.8	2.0	61.4	12.6
n-heptane → ethylcyclopentane + H_2	60.7	$10^{-6.3}$	60.6	$10^{-3.7}$	60.7	0.008	60.8	0.079	61.3	0.501	62.1	12.6
n-octane → *n*-propylcyclopentane + H_2	60.4	$10^{-6.3}$	60.3	$10^{-3.7}$	60.3	0.008	60.4	0.100	61.0	2.0	61.8	12.6
n-nonane → *n*-butylcyclopentane + H_2	60.8	$10^{-6.3}$	60.7	$10^{-3.7}$	60.7	0.008	60.8	0.079	61.3	2.0	62.8	12.6
Alkenes to five-membered cycloalkanes:												
1-pentene → cyclopentane	−56.4	$10^{7.0}$	−58.7	$10^{4.5}$	−60.3	1000	−61.4	79.4	−62.3	4.0	−62.2	0.631
1-hexene → methylcyclopentane	−65.1	$10^{9.0}$	−67.0	$10^{6.1}$	−68.3	$10^{4.3}$	−69.2	$10^{3.1}$	−69.7	39.8	−69.3	5.0
1-heptene → ethylcyclopentane	−64.8	$10^{8.9}$	−66.5	$10^{6.1}$	−67.8	$10^{4.3}$	−68.7	$10^{3.1}$	−69.2	39.8	−68.6	5.0
1-octene → *n*-propylcyclopentane	−65.2	$10^{9.0}$	−66.9	$10^{6.1}$	−68.2	$10^{4.3}$	−69.0	$10^{3.1}$	−69.5	39.8	−69.0	5.0
Alkanes to six-membered cycloalkanes:												
n-hexane → cyclohexane + H_2	44.1	$10^{-5.6}$	43.5	$10^{-3.7}$	43.5	0.003	44.1	0.016	46.3	1.6	49.6	0.631
n-heptane → methylcyclohexane + H_2	33.0	$10^{-3.3}$	33.1	0.150	33.8	0.100	34.9	0.158	38.1	2.0	42.0	7.9
n-octane → ethylcyclohexane + H_2	36.7	$10^{-4.0}$	36.9	0.004	37.7	0.040	38.9	5.0	42.4	1.6	46.4	5.0
n-nonane → *n*-propylcyclohexane + H_2	35.7	$10^{-3.9}$	36.2	0.005	37.2	0.040	38.6	0.200	42.3	1.6	46.3	5.0
n-decane → *n*-butylcyclohexane + H_2	36.5	$10^{-4.0}$	36.9	0.004	37.9	0.032	39.3	0.158	43.0	1.3	47.0	5.0
Alkenes to six-membered cycloalkanes:												
1-hexene → cyclohexane	−81.5	$10^{9.7}$	−83.7	$10^{6.1}$	−85.0	$10^{3.9}$	−85.4	251.2	−84.2	3.2	−81.2	0.316
1-heptene → methylcyclohexane	−92.5	$10^{11.9}$	−94.0	$10^{7.8}$	−94.7	$10^{5.0}$	−94.5	$10^{3.7}$	−92.4	50.1	−88.7	3.2
1-octene → ethylcyclohexane	−88.9	$10^{11.3}$	−90.3	$10^{7.4}$	−90.8	$10^{5.0}$	−90.5	$10^{3.4}$	−88.1	31.6	−84.3	2.5
1-decene → *n*-butylcyclohexane	−89.1	$10^{11.2}$	−90.3	$10^{7.3}$	−90.6	$10^{5.0}$	−90.1	$10^{3.4}$	−87.5	25.1	−83.7	2.0

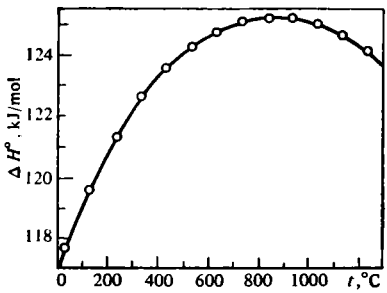


Fig. 32. Temperature dependence of the enthalpy of the reaction ethylbenzene → styrene + hydrogen

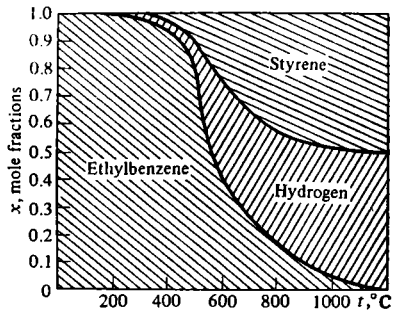


Fig. 33. Content of the reactants for the reaction ethylbenzene → styrene + hydrogen in an equilibrium gas phase for various temperatures and standard pressure

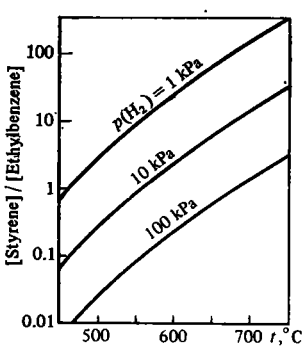


Fig. 34. Molar ratios of styrene and ethylbenzene in an equilibrium mixture for various temperatures and pressures

Examination of the above data reveals that dilution with hydrogen has the greatest influence at low equilibrium constants and degrees of conversion. If for some reason or other it is desirable to introduce hydrogen into the system, for example to retain the activity of the dehydrogenating catalyst, conditions should be chosen when high degrees of conversion of the feed stock are ensured.

In connection with the development of processes of the hydrofining and hydrocracking of high-molecular petroleum and coal fractions, equilibrium has been studied [60, 61] for the high pressures of hydrogenation reactions of bi- and polycyclic aromatics. A plot of log K_p° versus $1/T$ for a number of such reactions is given in Fig. 35. With a view to the non-ideal nature of the system, the data of Fig. 35 have been used to determine the compositions of the equilibrium mixture. Figures 36 and 37 give the equilibrium ratios of tetralins:naphthalenes and decalin:naphthalene for temperatures and pressures ranging from 300 to 500 °C and 3.5 to 10.5 MPa, respectively. It can be noted that the thermodynamic restrictions in the hydrogenation of alkyl derivatives grow. As for all hydrogenation reactions, low temperatures and high pressures are favourable. But if the selective hydrogenation of only a

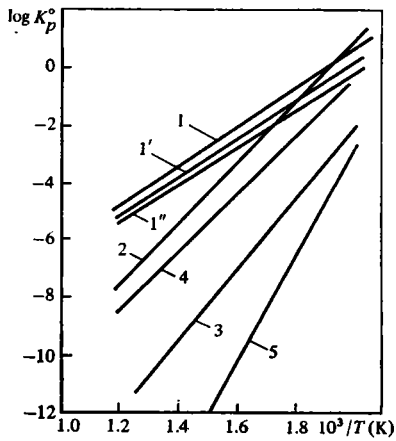


Fig. 35. Equilibrium constant versus $1/T$ for reactions of hydrogenation of polycyclic aromatic hydrocarbons:

1—naphthalene to tetralin; *1′*—alkylnaphthalene to alkyltetralin; *1″*—dialkylnaphthalene to dialkyltetralin; *2*—tetralin to decalin; *3*—phenanthrene to octahydrophenanthrene; *4*—octahydrophenanthrene to perhydrophenanthrene; *5*—chryzene to dodecahydrochryzene

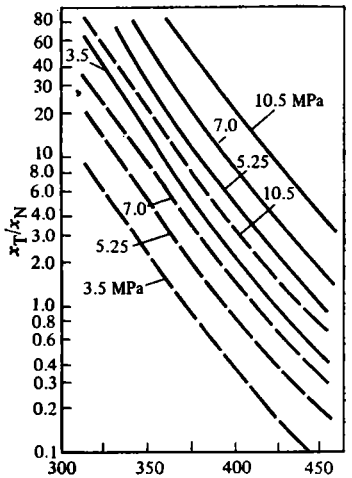


Fig. 36. Equilibrium ratio of tetralins to naphthalenes x_T/x_N for naphthalene (solid lines) and dialkylnaphthalene (dashed lines) for various temperatures and pressures of hydrogen (the numbers on the curves)

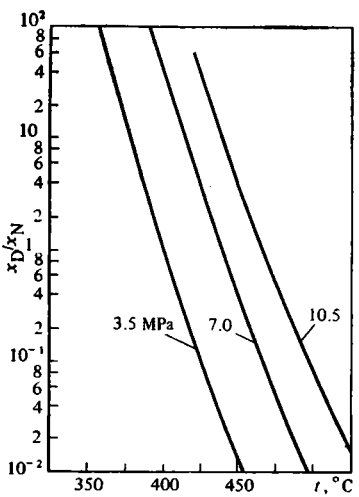


Fig. 37. Equilibrium ratio of decalin to naphthalene x_D/x_N for various temperatures and pressures of hydrogen (the numbers on the curves)

part of the aromatic rings is needed, one should use elevated temperatures and relatively low pressures of the hydrogen. Thus, at 400 °C and 3.5 MPa, the x_T/x_N ratio is 2.1, while the x_D/x_N ratio is 1.9. At the same time, the predominating formation of tetralins observed in experiments is explained by kinetic factors.

For high degrees of conversion in the hydrogenation of the first ring of polycyclic aromatics (phenanthrene, chryzene), moderate (up to 400 °C) temperatures and increased (>7 MPa) pressures of the hydrogen have to be employed. For the complete saturation of polycyclic aromatic compounds with high degrees of conversion, it is desirable to use pressures not below 7-10 MPa.

7.3. Reactions of Hydrogenolysis of C—C, C—S, C—O, and C—N Bonds

These reactions are used for freeing petroleum fractions and liquid coal-processing fractions of non-hydrocarbon components that prevent the direct use of the fractions for further treatment (they deactivate the catalyst), or contaminate the commercial product.

Data on the reactions of hydrogenolysis of C—C bonds in alkanes and cycloalkanes are given in Chap. 5. Here it should be noted that the hydrogenolysis of C—C bonds of an alkane chain at the ends and in the middle of a molecule is virtually equally probable thermodynamically, which is demonstrated by data for the hydrocracking of normal alkanes in the gas phase (Table 97).

Table 97. **Heats and Equilibrium Constants for Normal Alkane Hydrocracking Reactions**

Reaction	ΔH°_{800}, kJ	$\log K^\circ_p$ at T, K		
		500	800	1000
$C_{10}H_{22} + H_2 \rightarrow CH_4 + C_9H_{20}$	—62	$10^{6.4}$	$10^{4.3}$	$10^{3.3}$
$C_{10}H_{22} + H_2 \rightarrow C_2H_6 + C_8H_{18}$	—53	$10^{5.5}$	$10^{3.5}$	$10^{2.8}$
$C_{10}H_{22} + H_2 \rightarrow 2C_5H_{12}$	—53	$10^{5.6}$	$10^{3.6}$	$10^{2.9}$
$C_{10}H_{22} + H_2 \rightarrow 2$ *iso*-C_5H_{12}	—64	$10^{6.7}$	$10^{4.1}$	$10^{3.2}$

In hydrocracking, normal and isoalkanes form with a close thermodynamic probability, so that the breaking of the C—C bonds closer to the middle of a molecule and the formation of isomerized products are explained by kinetic (and not thermodynamic) factors. It is especially important that within a wide temperature range the hydrogenolysis of C—C bonds can proceed practically completely.

The thermodynamic characteristics of typical reactions of hydrogenolysis of C—S and C—O bonds are given in Table 98.

We shall note immediately that the hydrogenolysis of these bonds up to 800 K, and in the majority of cases up to 1000 K, is possible with very high degrees of conversion and is more probable thermodynamically than the hydrogenolysis of C—C bonds. Since, however, in practice it is necessary to purify hydrocarbons from compounds of sulphur, oxygen, and nitrogen in hydrogenation processes until the content of these substances is only a few millionths, we shall give data on the degrees of conversion in hydrogenolysis calculated by an equation relating K_x and y (see Table 91) (Table 99).

It is obvious that for high degrees of conversion of organo-element compounds, it is necessary to ensure high (preferably exceeding 100) H_2:feed stock ratios. If the content of the compound being removed in the fraction being processed is not large, for example, 1%, an H_2:fraction ratio equal to unity makes it possible to ensure a high degree of purification at $K_x > 10^3$.

In this connection, attention must be drawn to the fact that the hydrogenolysis of thiophene and also of its derivatives (the removal of the thiophene sulphur) should not be conducted at temperatures exceeding 500-600 K because the thermodynamic restrictions will be noticeable: at 800 K and $\delta(H_2) = 100$, the degree of conversion will not exceed 98%.

It should be noted that the evolution of heat in hydrogenolysis increases in the sequence C—C < C—S < C—O.

In hydrofining processes, the predominating hydrogenolysis of C—S, C—O, and C—N bonds in comparison with C—C ones is observed; attempts were repeatedly made to explain this by the different strength of these bonds. The mean values of the bond energies of the atoms in a molecule depend on its structure. The minimal values of these bond energies are as follows (in kJ/mol):

C—C	C—O	C—N	C—S
250	310	230	220

In the thermal action on a molecule, when the energy is uniformly distributed among all the bonds, the C—O bond is the most stable, while the others have approximately the same strength. Hence, the heating of petroleum or coal liquid fractions does not result in the removal of oxygen, nitrogen, and sulphur from them, but makes possible the redistribution of the heteroatoms between the molecules when the C—C bonds break.

The specific nature of catalytic action weakening selectively only definite bonds is taken into account by Balandin's multiplet theory [62]. The formation of a transition complex of the reactants with a catalyst is attended by the appearance of new bonds; here the

Table 98. **Heats $\Delta H°$ (in kJ) and Equilibrium Constants K_p° of Reactions of**

Reaction	Temperature, K		
	300		500
	$\Delta H°$	K_p°	$\Delta H°$
C—S bonds:			
$CH_3SH + H_2 \rightarrow CH_4 + H_2S$ (methanethiol)	—72.1	7.6×10^{12}	—74.4
$C_3H_7SH + H_2 \rightarrow C_3H_8 + H_2S$ (propanethiol)	—47.9	2.6×10^{9}	—51.4
$C_5H_{11}SH + H_2 \rightarrow C_5H_{12} + H_2S$ (pentanethiol)	—58.2	3.9×10^{10}	—61.1
$CH_3SC_3H_7 + 2H_2 \rightarrow CH_4 + C_3H_8 + H_2S$ (2-thiabutane)	—120.2	2.1×10^{22}	—126.7
$CH_3SC_4H_9 + 2H_2 \rightarrow CH_4 + C_4H_{10} + H_2S$ (2-thiapentane)	—108.6	1.1×10^{21}	—115.1
$C_2H_6S_2 + 3H_2 \rightarrow 2CH_4 + 2H_2S$ (2,3-dithiabutane)	—166.1	6.2×10^{31}	—174.9
$C_4H_{10}S_2 + 3H_2 \rightarrow 2C_2H_6 + 2H_2S$ (3,4-dithiahexane)	—135.2	7.6×10^{26}	—146.4
$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$ (thiophene)	—262.4	5.3×10^{30}	—273.0
$C_5H_6S + 4H_2 \rightarrow C_5H_{12} + H_2S$ (3-methylthiophene)	—257.8	2.9×10^{29}	—267.9
$C_4H_8S + 2H_2 \rightarrow C_4H_{10} + H_2S$ (thiacyclopentane)	—112.6	5.4×10^{16}	—116.5
$C_5H_{10}S + 2H_2 \rightarrow C_5H_{12} + H_2$ (thiacyclohexane)	—103.4	2.8×10^{16}	—107.3
C—O bonds:			
$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	—115.6	2.3×10^{20}	—116.7
$C_2H_5OH + H_2 \rightarrow C_2H_6 + H_2O$	—91.8	1.7×10^{16}	—93.8
$C_{10}H_{21}OH + H_2 \rightarrow C_{10}H_{22} + H_2O$	—88.3	4.5×10^{15}	—90.0

Hydrogenolysis of C—S and C—O Bonds Conducted in an Ideal Gas Phase

Temperature, K			Approximate dependence of K_p° on T for the temperature interval 300–800 K
500	800		
K_p°	ΔH°	K_p°	
6.3×10^{7}	—77.7	6.8×10^{4}	$K_p^\circ=\exp(-0.27+8980/T)$
9.5×10^{5}	—55.9	7.7×10^{3}	$K_p^\circ=\exp(0.94+6220/T)$
2.8×10^{6}	—66.6	9.0×10^{3}	$K_p^\circ=\exp(-0.50+7470/T)$
6.0×10^{13}	—135.3	4.7×10^{8}	$K_p^\circ=\exp(0.37+15\,310/T)$
2.0×10^{13}	—124.0	4.5×10^{8}	$K_p^\circ=\exp(2.06+13\,930/T)$
9.6×10^{19}	—187.1	8.4×10^{13}	$K_p^\circ=\exp(2.69+21\,160/T)$
1.4×10^{17}	—160.5	1.5×10^{11}	$K_p^\circ=\exp(2.85+17\,720/T)$
1.3×10^{12}	—283.6	18.5	$K_p^\circ=\exp(-38.64+32\,820/T)$
1.6×10^{11}	—277.0	3.5	$K_p^\circ=\exp(-39.36+32\,160/T)$
6.2×10^{8}	—121.8	1.4×10^{4}	$K_p^\circ=\exp(-7.74+14\,060/T)$
1.4×10^{9}	—117.0	6.3×10^{4}	$K_p^\circ=\exp(-5.92+13\,130/T)$
1.9×10^{12}	—119.0	4.8×10^{7}	$K_p^\circ=\exp(-0.02+14\,080/T)$
6.2×10^{9}	—97.0	1.2×10^{6}	$K_p^\circ=\exp(-0.37+11\,330/T)$
2.9×10^{9}	—92.4	7.8×10^{5}	$K_p^\circ=\exp(-0.09+10\,850/T)$

bonds that existed in the "free" molecule become weakened to a varying degree. The principles of geometric and energy consistence introduced by Balandin enable one to establish the structure of the transition complex and calculate the energies of the bonds of the atoms in it by conventional thermodynamic procedures.

Table 99. **Equilibrium Degrees of Conversion in the Hydrogenolysis of C—S, C—O, and C—N Bonds**

H_2:feed stock ratio	Equilibrium constant K_x	Equilibrium degree of feed stock conversion y, %
1	10	75.97
	10^3	96.93
	10^4	99.00
	10^5	99.90
10	10	98.91
	10^3	99.990
	10^4	99.9980
	10^5	99.9999...
100	10	99.90
	10^3	99.9990
	10^4	99.9999...
1000	10	99.994
	10^3	99.9999...

Thus, owing to the formation of bonds with nickel in a nickel-containing catalyst, the bond energies in the transition complex (in kJ/mol) are as follows:

C—C	C—N	C—S	C—O
205	110	21	17

It is clear that the nickel catalyst removes the oxygen, sulphur, and nitrogen while retaining the hydrocarbon chains. Therefore the calculations of the bond energies in a transition complex using Balandin's theory allows us to foresee catalytic activity on the basis of thermodynamic calculations.

7.4. Thermodynamic Analysis of Some Industrially Important Reactions

Many guides and articles give the equilibrium degrees of conversion, ΔG°, and ΔH° of reactions with the participation of hydrogen [4, 26]. It must be borne in mind that although the data on ΔG° and ΔH° are generally accurate, it is difficult to use the calculations of the degrees of conversion because they are given for definite temperatures and pressures, but not for hydrogen:feed stock

ratios. For a specific situation $[T, p, \delta(H_2)]$, it is better to resort to calculations as is done below.

Hydrogenation of Benzene to Cyclohexane. This reaction is employed for the production of cyclohexane. For this reaction $\gamma^\circ(C_6H_6) \approx \approx \gamma^\circ(C_6H_{12})$, and in accordance with the data of Tables 91, 93-96, we have:

$$K_{\gamma^\circ} \approx 1, \; K_x = K_p^\circ \left(\frac{p}{p^\circ}\right)^3 = \left(\frac{p}{p^\circ}\right)^3 \times \exp\left(-46.9 + \frac{25\,760}{T}\right)$$

Below are given the values of K_x for various temperatures and pressures:

Temperature, K		400			500	
Pressure, MPa	0.1	1	10	0.1	1	10
log K_x	7.6	8.6	9.6	2.0	3.0	4.0
Temperature, K		600			800	
Pressure, MPa	0.1	1	10	0.1	1	10
log K_x	−1.7	−0.7	0.3	−6.4	−5.4	−4.4

The relation between K_x and the degree of conversion of the feed stock y by Table 91 in the absence of the product in the initial mixture is

$$K_x = \frac{y(1+\delta_{H_2}-3y)^3}{(1-y)(\delta_{H_2}-3y)^3}$$

At temperatures up to 500 K and low pressures and hydrogen: feed stock ratios, practically complete conversion can be achieved. Thus, at $\delta(H_2) = 3$ (the stoichiometric amount) and $y = 0.99$, we obtain $\log K_x = 6.6$, while at $\delta(H_2) = 5$ and $y = 0.99$, we find $\log K_x = 2.5$. If, however, from kinetic considerations the hydrogenation catalyst requires the use of elevated temperatures (for example, sulphide catalysts are active at 600 K and higher), then high degrees of conversion are possible only at high pressures and hydrogen:feed stock ratios. Thus, at 600 K and a pressure of 10 MPa, degrees of conversion exceeding about 80% are impossible even at $\delta(H_2)$ close to 20 (industrial conditions). One can use Fig. 31*e* for specific determinations of the degree of conversion for various values of K_x and $\delta(H_2)$.

Dehydrogenation of Six-Membered Cycloalkanes. These reactions are carried out in platforming under conditions of elevated temperatures, high pressures, and dilution with hydrogen. The published data do not take account of the influence of the values of $\delta(H_2)$ on the degree of conversion. For these reactions (at a pressure under 5 MPa), $K_{\gamma^\circ} = 1$, and the following relations hold in accordance with the data in Tables 91 and 93:

$$K_x = K_p^\circ (p^\circ/p)^3 = \begin{cases} (p^\circ/p)^3 \exp[-(-46.9 + 25\,760/T)], & n = 6 \\ (p^\circ/p)^3 \exp[-(-46.8 + 25\,400/T)], & n = 7 \\ (p^\circ/p)^3 \exp[-(-47.3 + 24\,110/T)], & n = 8 \end{cases}$$

Below are given the values of K_x for temperatures of 700 and 800 K that are of interest for an industrial process:

Temperature, K	700			800		
Pressure, MPa	0.1	2	4	0.1	2	4
K_x for dehydrogenation of cycloalkanes:						
with 6 carbon atoms	4.4	3.1	2.8	6.4	5.1	4.8
with 7 carbon atoms	4.6	3.3	3.0	6.5	5.2	4.9
with 8 carbon atoms	5.6	4.3	4.0	7.4	6.1	5.8

Let us determine the possible equilibrium degree of conversion of cyclohexane. We shall take into consideration that the hydrogen:feed stock ratio in platforming is about five (for an industrial process), while the hydrogen:cyclohexane ratio can be larger by an order of magnitude: $\delta(H_2) = 50$. From the equation holding in the absence of benzene in the initial mixture (see Sec. 1.7), we find that already at 700 K dehydrogenation is possible practically to the end. Even if the initial mixture does contain benzene, as happens in an industrial process, for example, $\delta_{A'} = 1$, in this case too the conversion of over 99% of the cyclohexane to benzene is possible. There are also no thermodynamic restrictions for six-membered cycloalkanes with seven and more carbon atoms because their dehydrogenation equilibrium constants are larger than those of benzene.

Hydrodealkylation of Toluene. The reaction

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$$

is used to increase the production of benzene, it is conducted at high (>800 K) temperatures. The equilibrium constants of this reaction are $K^\circ_{p,800} = 10^{2.6}$ and $K^\circ_{p,1000} = 10^2$. The following expression relates K_x and the equilibrium degree of conversion y:

$$K_x = \frac{y(\delta_{A'} + y)}{(1-y)(\delta_{H_2} - y)}$$

where $\delta_{A'}$ is the benzene:toluene molar ratio in the initial mixture.

This signifies that the following degrees of conversion are possible:

Temperature, K	800					
$\delta(H_2)$	1		4		10	
$\delta_{A'}$	0	1	0	1	0	1
y, fractions	0.95	0.93	0.99	0.99	0.99	0.99

Temperature, K	1000					
$\delta(H_2)$	1		4		10	
$\delta_{A'}$	0	1	0	1	0	1
y, fractions	0.91	0.87	>0.99	0.99	>0.99	0.99

It is obvious that at $\delta(H_2) = 4$ and more, the thermodynamic restrictions to the conversion of toluene can be eliminated. This

is exactly what is resorted to in the industry [$\delta(H_2) > 4$], which also makes it possible to suppress the side reactions of condensation.

Hydrodealkylation of Alkylnaphthalenes. The reaction

$$C_{10}H_{8-\nu}(R)_\nu + \nu H_2 \rightarrow C_{10}H_8 + \nu RH$$

is used to produce naphthalene from the alkylnaphthalene fraction of catalytic cracking gas oils. It is conducted at temperatures of 900-1000 K, at pressures of 6-7 MPa, and $\delta(H_2)$ up to 10. Let us estimate the thermodynamic restrictions in the hydrodealkylation of 1-methyl- and 1-ethylnaphthalenes. We shall take into account that since $\gamma^\circ(C_{10}H_7{-}R) \approx \gamma^\circ(C_{10}H_8)$, then $K_{\gamma^\circ} \approx 1$. The logarithms of the equilibrium constants are given below:

Hydrodealkylation feed stock	1-Methylnaphthalene	1-Ethylnaphthalene	1,3-Dimethylnaphthalene	2-Ethyl-3-methylnaphthalene
log K_x at temperatures, K:				
900	2.63	2.0	5.8	4.9
1000	2.3	1.8	5.2	4.4

At values of K_x exceeding $10^{1.8} = 63.1$ and $\delta(H_2) > 5$, the equilibrium degrees of conversion exceed 99%, i.e. there are no thermodynamic restrictions in industrial processes. It should be noted that if the ratio H_2:alkylnaphthalene were taken equal to unity, the equilibrium degree of conversion of 1-ethylnaphthalene (the least favourable feed stock from thermodynamic considerations) at 1000 K would be 89%, i.e. the thermodynamic restrictions would be noticeable.

Dehydrogenation of C_4 and C_5 Alkanes and Alkenes. Dehydrogenation is performed to produce dienes (more rarely, alkenes) in one or two steps, i.e. by combining or separating the steps of producing an alkene and a diene. Reduced pressures are employed to increase the yield of the target product. For the temperature interval 700-1000 K, which is of interest for industrial applications, the following equations can be used to evaluate K_x:

Reaction	Equation
Butane → H_2 + 1-butene	$\log K_x = \log (p^\circ/p) + 6.56 - 6310/T$
1-Butene → H_2 + 1,3-butadiene	$\log K_x = \log (p^\circ/p) + 6.78 - 6590/T$
Isopentane → H_2 + 1-isopentene	$\log K_x = \log (p^\circ/p) + 6.88 - 5970/T$
1-Isopentene → H_2 + isoprene	$\log K_x = \log (p^\circ/p) + 6.77 - 6670/T$

There are no fundamental difficulties in calculating the equilibrium degrees of conversion of a simple or complex dehydrogenation reaction when the values of K_x are known. If a simple reaction proceeds and the initial mixture contains no hydrogen, the degree of conversion y of the feed stock is determined from the equation

$$K_x = \frac{y^2}{1-y^2} \quad \text{or} \quad y = \sqrt{\frac{K_x}{1+K_x}}$$

Table 100. **Equilibrium Degrees of Conversion and Yields of Dienes in the Dehydrogenation of *n*-Butane and Isopentane**

Reaction	T, K	$p°/p$	Degree of conversion of alkane or alkene, fractions		Yield of diene, fractions	
			C_4	C_5	C_4	C_5
Alkane → H_2 + alkene	700	1	0.06	0.15	—	—
		2	0.08	0.24	—	—
		10	0.14	0.43	—	—
Alkene → H_2 + diene	700	1	—	—	0.05	0.04
		2	—	—	0.06	0.05
		10	—	—	0.15	0.12
Alkane → H_2 + alkene → H_2 + diene	700	1	0.06	0.15	0.002	0.002
		2	0.08	0.24	0.004	0.004
		10	0.14	0.43	0.02	0.02
Alkane → H_2 + alkene	800	1	0.21	0.45	—	—
		2	0.30	0.58	—	—
		10	0.58	0.85	—	—
Alkene → H_2 + diene	800	1	—	—	0.17	0.16
		2	—	—	0.25	0.23
		10	—	—	0.51	0.46
Alkane → H_2 + alkene → H_2 + diene	800	1	0.22	0.45	0.03	0.04
		2	0.31	0.60	0.06	0.07
		10	0.63	0.89	0.27	1.29

Table 100 (*concluded*)

Reaction	T, K	p°/p	Degree of conversion of alkane or alkene, fractions		Yield of diene, fractions	
			C_4	C_5	C_4	C_5
Alkane → H_2+alkene	900	1	0.54	0.85	—	—
		2	0.64	0.88	—	—
		10	0.86	0.97	—	—
Alkene → H_2+diene	900	1	—	—	0.47	0.43
		2	—	—	0.61	0.56
		10	—	—	0.86	0.82
Alkane → H_2+alkene → H_2+diene	900	1	0.56	0.83	0.22	0.25
		2	0.74	0.92	0.38	0.41
		10	0.96	0.98	0.79	0.65
Alkane → H_2+alkene	1000	1	0.80	0.95	—	—
		2	0.87	0.97	—	—
		10	0.98	~1	—	—
Alkene → H_2+diene	1000	1	—	—	0.77	0.75
		2	—	—	0.88	0.85
		10	—	—	0.97	0.98
Alkane → H_2+alkene → H_2+diene	1000	1	0.91	0.97	0.65	0.65
		2	0.99	0.99	0.75	0.75
		10	~1	~1	0.95	0.95

For the complex reaction

$$\text{alkane} \xrightarrow{K_{x_1}} H_2 + \text{alkene} \xrightarrow{K_{x_2}} H_2 + \text{diene} \qquad \text{(XXIII)}$$

denoting the degree of conversion of the alkane by y_1 and the yield of the diene (the mole fraction of the alkane) by y_2, we obtain the following system of equations when the initial mixture contains no hydrogen nor alkene:

$$K_{x_1} = \frac{y_1^2 - y_2^2}{(1-y_1)(1+y_1+y_2)}, \quad K_{x_2} = \frac{y_2(y_1+y_2)}{(y_1-y_2)(1+y_1+y_2)}$$

We have performed calculations of the equilibrium compositions of simple and complex reactions with the use of methods described in Chap. 3 and of standard search programmes for computers. Some of the results of the calculations are given in Table 100.

It can be seen from the data in Table 100 that from thermodynamic considerations at moderate temperatures, a two-step process is expedient, i.e. the separate carrying out of dehydrogenation of the alkane and alkene. Even under conditions of high degrees of conversion of the alkane and alkene with their separate dehydrogenation, the conducting of a complex reaction with the simultaneous production of an alkene and diene encounters thermodynamic restrictions due to the increased hydrogen content in the equilibrium mixture. Thermodynamic restrictions are absent only at temperatures above 1000 K or at 1000 K and a pressure in the system of about 0.01 MPa.

When using the data of Table 100, as well as the obsolete data of Brooks *et al.* cited in the literature (see [4]), one must have in view that if several alkenes form simultaneously, for example, *cis*- and *trans*-alkenes with an internal double bond, the degree of conversion of the alkane and the yield of the diene will be somewhat higher than the values indicated in Table 100.

For example, if at 800 K and $p^\circ/p = 1$ two alkenes with close equilibrium constants form, then the degree of conversion of the alkane is not 0.21 (the value given in the table for butane), but 0.29; the yield of the diene in the complex reaction is not 0.03 (the value in Table 100), but 0.05 mol per mol of alkane, i.e. it will be about 1.7 times larger. Hence, in thermodynamic calculations of real processes, one must take into consideration which alkenes form from the alkane and perform the calculations of equilibrium for all possible simple reactions relating both to the dehydrogenation of the alkane and to the dehydrogenation of the alkene.

Chapter 8

Production of Synthesis Gas and Syntheses Based on CO and CO_2

8.1. Production of Synthesis Gas

The production of synthesis gas (CO and H_2) is based on the conducting of endothermic reactions of carbon-containing substances and steam:

$$C_s + H_2O \rightarrow CO + H_2 \qquad \text{(XXIV)}$$

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)\,H_2 \qquad \text{(XXV)}$$

The difference between reactions (XXIV) and (XXV) consists in that at the reaction temperature C_s is a solid, whereas C_nH_m is a gas. At present, methane is the main hydrocarbon used as the feed stock. The temperature of producing synthesis gas is chosen from kinetic considerations; it does not exceed 1500 K.

The ratio of CO and H_2 is affected not only by the composition of the feed stock [i.e. the primary reactions (XXIV) and (XXV)], but also by the proceeding of secondary reactions:

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$CO_2 + C_s \rightarrow 2CO$$

$$C_s + 2H_2 \rightarrow CH_4$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Conversion is sometimes carried out with small amounts of oxygen present to allow partial oxidation to compensate for the absorption of heat by the main process. This is why the role of the reactions of coal and hydrocarbons with oxygen resulting in the formation of CO, CO_2, and H_2O is considered in thermodynamic analysis. The thermodynamic analysis of combustion reactions is customarily associated with the possibility of the dissociation of molecules of oxygen, hydrogen, and water into atoms and of other reactions (see Chap. 4).

Let us consider data on the reactions that can proceed in the production of synthesis gas. Table 101 presents the heats and equilibrium constants of the reactions whose proceeding seems to be possible. Let us consider the data on these reactions.

Combustion Reactions. Some information on these reactions is also given in Chap 4. We shall note the following. The decomposition of H_2, O_2, and H_2O into atoms and hydroxyl ions at temperatures up to 1500 K does not practically occur. The molecular combustion

reactions proceed to the end. This is why the decomposition of molecules with the evolution of molecular oxygen can be disregarded. The equilibrium composition of the combustion products is determined by the proceeding of secondary reactions. We shall therefore give the results of calculating the composition of the products [4, 20, 61].

Table 101. **Heats ΔH°_{298} and Equilibrium Constants K°_p of Reactions Proceeding in the Production of Synthesis Gas**

Reaction	ΔH°_{298}, kJ	K°_p at temperatures, °C	
		800	1300
$C + O_2 \rightarrow CO_2$	—406.4	1.8×10^{17}	1.5×10^{13}
$2C + O_2 \rightarrow 2CO$	—246.4	1.4×10^{18}	4.5×10^{16}
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	—715	10^{40}	10^{30}
$C + CO_2 \rightarrow 2CO$	—160.9	7.64	3×10^3
$C + H_2O \rightarrow CO + H_2$	118.9	7.97	9.98
$C + 2H_2O \rightarrow CO_2 + 2H_2$	16.3	8.31	3.3×10^2
$C + 2H_2 \rightarrow CH_4$	—83.8	4.7×10^{-2}	1.8×10^{-3}
$2CO + O_2 \rightarrow 2CO_2$	—567.3	2.4×10^{14}	5.0×10^9
$2H_2 + O_2 \rightarrow 2H_2O$	—482.2	2.2×10^{16}	4.5×10^{16}
$CO + H_2O \rightarrow CO_2 + H_2$	—42.4	1.04	0.33
$CO + 3H_2 \rightarrow CH_4 + H_2O$	—206.7	5.92×10^{-3}	1.82×10^{-6}
$2CO_2 + 2H_2 \rightarrow CH_4 + CO_2$	—248.4	6.17×10^{-3}	6.05×10^{-7}

1. When air is blown through a coal bed, what is called air-producer gas is obtained by the reactions $C + O_2 \rightarrow CO_2$, $C + 0.5O_2 \rightarrow CO$, and $C + CO_2 \rightarrow 2CO$ (the latter reaction is a dependent one). The equilibrium composition of air-producer gas at moderate temperatures is as follows:

Temperature, °C	650	800	1000
Content of components, mole fractions:			
N_2	0.72	0.66	0.66
CO_2	0.11	0.02	0.002
CO	0.17	0.32	0.34

2. If carbon dioxide is blown through a bed of coal, equilibrium sets in between the CO and CO_2 as a result of proceeding of the Boudoir reaction $C + CO_2 \rightarrow 2CO$. The equilibrium between the gaseous components of this reaction is as follows:

Temperature, °C	450	550	650	800	925
Content of components, mole fractions:					
CO	0.005	0.11	0.60	0.93	0.96
CO_2	0.995	0.89	0.40	0.07	0.04

Reactions of Methane Formation. Methane can form in the hydrogenation of C, CO, and CO_2.

1. The ratio of the equilibrium partial pressures of methane and hydrogen in the formation of CH_4 from graphite and hydrogen has been determined in [53] and is presented in Table 102.

Table 102. **Ratio of Equilibrium Partial Pressures of Methane and Hydrogen When Methane Forms from Graphite and Hydrogen**

Temperature, °C	$x(CH_4) \times 10^3$ at standard pressure	Ratio of partial pressures at total pressure in system, MPa			
		0.01	0.1	1.0	10
300	92.3	15.5	155	1550	15500
400	76.2	1.35	13.5	135	1350
500	49.2	0.19	1.9	19	190
600	24.4	4×10^{-2}	0.4	4.3	43
700	10.8	1.4×10^{-2}	0.1	1.3	13
800	4.8	5×10^{-3}	0.05	0.5	5.3
900	2.3	2×10^{-3}	0.02	0.2	2.4
1000	1.2	1×10^{-3}	0.01	0.1	1.3

2. For the reaction $CO + 3H_2 \rightarrow CH_4 + H_2O$, the approximate temperature dependence of the equilibrium constant has the form

$$\log K_p^\circ = -12.90 + \frac{11\,495}{T}$$

At temperatures below 300 °C, the equilibrium constant exceeds 10^3, while at temperatures above 600 °C it is less than 0.8. The methane content in the products of this reaction depends on the content of CO, H_2, and H_2O in the initial mixture, the temperature, and the pressure in the system. This is why calculations are needed for each specific set of the enumerated quantities based on the equation

$$K_x = K_p^\circ \left(\frac{p}{p^\circ}\right)^2$$
$$= \frac{[\delta(CH_4)+y]\ [\delta(H_2O)+y]\ [1+\delta(H_2)+\delta(CH_4)+\delta(H_2O)-2y]^2}{(1-y)\,[\delta(H_2)-3y]^3}$$

If, for example, $\delta(H_2)/\delta(CO) = 3$, $\delta(H_2O)/\delta(CO) = 1$, and $\delta(CH_4) = 0$, then at temperatures below 300 °C degrees of conversion exceeding 95% are possible, while at temperatures above 600 °C they will be below 5%, in other words, not over 5% of CO can transform into methane. Also having in view that the formation of methane by this reaction is suppressed by the presence of water vapour (steam) in the reaction mixture, we can conclude that at temperatures above 800 °C the role of this reaction will be insignificant.

3. For the reaction $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, the approximate temperature dependence of the equilibrium constant has the

form:

$$\log K_p^\circ = -11.10 + \frac{9585}{T}$$

This constant is lower than that of the reaction by which methane is produced from CO. Since the content of CO_2 in the reaction mixture is not large, while the presence of water vapour suppresses the formation of methane by this reaction especially greatly, its role at temperatures above 800 °C can be disregarded.

Reactions of Producing Synthesis Gas by Reacting H_2O *with Carbon and* CH_4.

1. When conducting the reaction $C_s + H_2O \rightarrow CO_2 + H_2$ by blowing steam through coke, the following equilibrium mixtures form ($p/p^\circ = 1$):

Temperature, K	600	700	800	900	1000	1100	1200
K_p°	5×10^{-5}	2.4×10^{-3}	4.4×10^{-2}	0.4	2.6	11.6	39.8
Content in equilibrium mixture, % (mol.):							
H_2O . . .	98.6	90.7	66.0	29.4	8.0	2.0	0.6
CO . . .	0.7	4.65	17.0	35.3	46.0	49.0	49.7
H_2	0.7	4.65	17.0	35.3	46.0	49.0	49.7

It is obvious that for high degrees of conversion of the steam, the temperature of the process must not be lower than 700-800 °C.

2. For the steam conversion of methane $CH_4 + H_2O \rightarrow CO + 3H_2$, the composition of the equilibrium mixture is determined not only by the temperature and pressure, but also by the methane: steam ratio. When the initial mixture contains no CO and H_2, the equilibrium constant and the degree of conversion of the methane are related by the expression:

$$K_x = K_p^\circ \left(\frac{p^\circ}{p}\right)^2 = \frac{27y^4}{(1-y)\,[\delta(H_2O)-y]\,[1+\delta(H_2O)+2y]^2}$$

At standard pressure and a methane:steam ratio equal to unity, the following compositions of the gas mixture can be obtained:

Temperature, K	700	800	900	1000	1100	1200
K_p°	2.7×10^{-4}	3.1×10^{-2}	1.3	25.6	313	2473
Content in equilibrium mixture, % (mol):						
CH_4	42.7	29.8	14.4	5.1	1.7	0.6
H_2O	42.7	29.8	14.4	5.1	1.7	0.6
CO	3.7	10.1	17.8	22.5	24.1	24.7
H_2	10.9	30.3	53.4	67.3	72.5	74.1

As when dealing with coke, in the given case the practically complete conversion of the methane requires temperatures of at least 700-800 °C. But by increasing the steam:methane ratio $\delta(H_2O)$,

one can also increase the degree of conversion of methane at lower temperatures. For example, at 800 K and $\delta(H_2O) = 1$, the degree of conversion of methane is about 70%. If at the same temperature one uses five-fold dilution of the methane with steam, i.e. $\delta(H_2O) = 5$, the degree of conversion is 92%.

3. Here we shall also give data on the degree of conversion of CO because this reaction ($CO + H_2O \rightarrow CO_2 + H_2$) results in the production of additional amounts of hydrogen. The results of this reaction are affected by the temperature and the composition of the initial mixture. The equation relating the degree of conversion of the CO, i.e. y to the equilibrium constant and the ratios of the components in the initial mixture $m(H_2O):m_0(CO) = \delta(H_2O)$, $m_0(CO_2):m_0(CO) = \delta(CO_2)$, and $m_0(H_2):m_0(CO) = \delta(H_2)$ is as follows:

$$K_x = K_p^\bullet = \frac{[\delta(CO_2)+y]\,[\delta(H_2)+y]}{(1-y)\,[\delta(H_2O)-y]}$$

Below are given data on the content of the components in an equilibrium gas mixture at $\delta(H_2O) = 1$ and $\delta(CO_2) = \delta(H_2) = 0$:

Temperature, K	500	600	700	800	900	1000	1100	1200	1500
$K_p^\bullet$	126	27	9.0	4.0	2.2	1.4	0.95	0.70	0.37
Content in equilibrium mixture % (mol):									
CO	4.1	8.1	12.5	16.6	20.1	23.0	25.4	27.3	31.1
H_2O . . .	4.1	8.1	12.5	16.6	20.1	23.0	25.4	27.3	31.1
H_2	45.9	41.9	37.5	33.4	29.9	27.0	24.6	22.7	19.9
CO_2	45.9	41.9	37.5	33.4	29.9	27.0	24.6	22.7	19.9

It is obvious that the conversion of the CO proceeds within a broad range of temperatures and will noticeably affect the composition of the equilibrium mixture in a complex conversion process. It is also clear that the degree of conversion of the CO in the reaction drops when $\delta(CO_2)$ and $\delta(H_2)$ grow and when $\delta(H_2O)$ decreases.

The above treatment of the simple reactions proceeding in the production of synthesis gas facilitates the analysis of complex equilibrium when all these reactions (or part of them) proceed simultaneously.

When considering complex equilibrium (the simultaneous proceeding of the reactions characterized above), we can find the composition of the equilibrium mixture. It must be had in view, however, that it is determined by the composition of the initial mixture (the $H_2O:O_2$ ratio), the pressure, and temperature. This is why the number of possible equilibrium compositions is large. But that the content of CO and H_2 in an equilibrium mixture grows and the content of CO_2, H_2O, and CH_4 decreases is always true. For purposes of illustration, below we give two examples of calculations.

Example 1. Coal is treated with a mixture of H_2O and O_2 at 298 K. The reactions $C + O_2 \rightarrow CO_2$ and $C + H_2O \rightarrow CO + H_2$ proceed simultaneously. What must the ratio $H_2O:O_2$ in the initial mixture be for the process to be isothermal?

Using the heats of the reactions given in Table 101, we find that for compensation of the absorption of heat in the conversion of one mole of carbon (118.6 kJ), it is necessary to oxidize 118.6/406.4 = 0.29 mol of C. Hence, the molar ratio $H_2O:O_2$ must be 1:0.29, and the ratio $H_2O:O_2:C$ must be 1:0.29:1.29 (mol.).

Example 2. Coal is treated with a mixture of H_2O and O_2 in the ratio 1:0.2 at 0.1 MPa and 700 °C. Determine the composition of the equilibrium mixture, taking into account the simultaneous proceeding of oxidation and conversion reactions (the latter reactions are characterized in Table 101).

Since the oxidation of C to CO_2 proceeds virtually to the end, it is sufficient to consider the equilibrium of the reactions characterized in Table 101 if the $H_2O:CO_2$ ratio in the initial mixture is 1:0.2 (the oxygen passes over into the CO_2). The following relations hold (m_i is the number of moles in the equilibrium mixture):

$$K_{p_1} = \frac{[p(CO)]^2}{p(CO_2)} = \frac{[m(CO)]^2}{m(CO_2)\sum m}\,p \qquad \text{(a)}$$

$$K_{p_2} = \frac{p(CO)\,p(H_2)}{p(H_2O)} = \frac{m(CO)\,m(H_2)}{m(H_2O)\sum m}\,p \qquad \text{(b)}$$

$$K_{p_3} = \frac{p(CH_4)}{[p(H_2)]^2} = \frac{m(CH_4)\sum m}{[m(H_2)]^2 p} \qquad \text{(c)}$$

$$K_{p_4} = \frac{p(H_2)\,p(CO_2)}{p(CO)\,p(H_2O)} \qquad \text{(d)}$$

where $\sum m = m(CO) + m(CO_2) + m(H_2) + m(H_2O) + m(CH_4)$. If $m_0(H_2O)$ is the initial number of moles of water vapour (steam), then since the number of moles of hydrogen and oxygen is retained, we obtain the additional conditions (see Chap. 3):

$$m_0(H_2O) = m(H_2) + m(H_2O) + 2m(CH_4) \qquad \text{(e)}$$

$$\frac{1}{2}\,m_0(H_2O) + m_0(CO_2) = m(CO_2) + \frac{1}{2}\,m(CO) + \frac{1}{2}\,m(H_2O) \qquad \text{(f)}$$

By solving the above system of equations (a)-(f), we find the five unknown values of m_i. It should be noted that equations (a), (b), and (d) are dependent: the ratio of (b) and (d) yields (a). With this in view, let us consider the calculations for the case when the initial mixture contained 1 mol of H_2O and 0.2 mol of O_2 or after the oxidation of 1 mol of H_2O and 0.2 mol of CO_2.

Using the equilibrium constants K_x calculated from K_p and excluding the dependent equation (d), we have:

$$0.6 = \frac{[m(CO)]^2}{m(CO_2)\sum m}, \quad 1.8 = \frac{m(CO)\,m(H_2)}{m(H_2O)\sum m}, \quad 2.8 = \frac{m(CH_4)\sum m}{[m(H_2)]^2}$$

$$1 = m(H_2) + m(H_2O) + m(CH_4)$$

$$0.5 + 0.2 = m(CO_2) + \frac{1}{2}\,m(CO) + \frac{1}{2}\,m(H_2O)$$

This system of five independent equations contains five unknowns. To solve it, we consecutively exclude $m(H_2O)$ and $m(CO_2)$. We obtain the following

system:

$$0.6 = \frac{[m\,(CO)]^2}{\left[0.2 - \frac{1}{2}\,m\,(CO) + \frac{1}{2}\,m\,(H_2) + m\,(CH_4)\right]\left[1.2 + \frac{1}{2}\,m\,(H_2) + \frac{1}{2}\,m\,(CO)\right]}$$

$$1.8 = \frac{m\,(CO)\,m\,(H_2)}{[1 - m\,(H_2) - 2m\,(CH_4)]\left[1.2 + \frac{1}{2}\,m\,(H_2) + \frac{1}{2}\,m\,(CO)\right]}$$

$$2.8 = \frac{m\,(CH_4)\left[1.2 + \frac{1}{2}\,m\,(H_2) + \frac{1}{2}\,m\,(CO)\right]}{[m\,(H_2)]^2}$$

By solving this system using one of the search methods (see [8]), we find that a sufficiently good approximation is achieved when $m(CO) = 0.58$, $m(CH_4) = 0.41$, $m(H_2) = 0.15$, $m(H_2O) = 0.03$, and $m(CO_2) = 0.395$.

Calculations of Complex Equilibrium for the Reaction of Coal with Steam. The above treatment shows that if coal is converted at moderate temperatures by reaction with steam or its mixture with oxygen (or air), we can go over to calculating the degrees of conversion of equivalent amounts of $C\text{-}H_2O\text{-}CO\text{-}CO_2$ or $C\text{-}H_2O\text{-}CO\text{-}CO_2\text{-}N_2$ mixtures, i.e. consider that the oxygen was consumed for the formation of CO and (or) CO_2. Here the following reactions are possible:

$$C + H_2O \rightarrow CO + H_2 \qquad (1)$$

$$C + 2H_2 \rightarrow CH_4 \qquad (2)$$

$$C + CO_2 \rightarrow 2CO \qquad (3)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (4) = -(1) + (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (5) = -2\,(1) + (2) + (3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (6) = (1) - (3)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (7) = (3) - (2)$$

Only three of these seven reactions are independent. It is shown above which combinations of reactions (1)-(3) allow us to obtain reactions (4)-(7). Therefore in thermodynamic analysis, it is sufficient to consider the equilibrium only of reactions (1)-(3). To calculate the equilibrium composition, we can use the method described in Chap. 2—go over to the numbers of moles m_i of the components. Let us assume that $m_0(H_2O)$ moles of H_2O, $m_0(CO)$ moles of CO, and $m_0(CO_2)$ moles of CO_2 react with the coal, and the number of moles of the i-th component in equilibrium is m_i. Let the sum of the moles of the components in equilibrium be

$$\sum m_i = m(H_2O) + m(CO) + m(CO_2) + m(H_2) + m(CH_4)$$

Hence, to determine the five unknown m_i's (the number of moles of nitrogen does not change), we have five equations:

$$K_{x(1)} = \frac{m(CO_2)\, m(H_2)}{m(H_2O) \sum m_i}$$

$$K_{x(2)} = \frac{m(CH_4) \sum m_i}{[m(H_2)]^2}$$

$$K_{x(3)} = \frac{[m(CO)]^2}{m(CO_2) \sum m_i}$$

$$m_0(H_2O) = m(H_2) + 2m(CH_4) + m(H_2O) \quad \text{(hydrogen balance)}$$

$$m_0(H_2O) + m_0(CO) + 2m_0(CO_2) = m(H_2O) + m(CO) + 2m(CO_2)$$

(oxygen balance)

The equilibrium constants can be calculated by approximate equations holding for the temperature interval 800-1200° K:

$$\log K_{x(1)} = \log\left(\frac{p^\circ}{p}\right) + 7.54 - \frac{7120}{T}$$

$$\log K_{x(2)} = \log\left(\frac{p}{p^\circ}\right) - 5.60 + \frac{4600}{T}$$

$$\log K_{x(3)} = \log\left(\frac{p^\circ}{p}\right) + 9.28 - \frac{9000}{T}$$

Solution of the system of five equations by any of the search methods described earlier enables us to find an equilibrium set of m_i's. It is clear that the solution depends on the temperature, pressure, and initial amounts of the components. An example of the calculations is given on a previous page.

Calculations of Complex Equilibrium for the Reaction of Methane with Steam. If a mixture of steam and oxygen enters into the reaction, then as for coal, one should go over to calculations of the degrees of conversion of equivalent amounts of the mixture CH_4-H_2O-CO-CO_2, assuming that the oxygen is spent on oxidation. Thermodynamically, the same seven reactions are possible as for coal, but only three of them are independent. In this case, it is convenient to choose the following reactions as the independent ones [in writing the stoichiometric equation of reaction (4), below we have exchanged the places of the right-hand and left-hand sides]:

$$C + CO_2 \rightarrow 2CO \tag{3}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{4}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

By expressing the equilibrium constants of these reactions in terms of the number of moles of the components in the equilibrium mixture and writing down the hydrogen and oxygen balances, we obtain,

as previously, five equations for determining the five unknown values of m_i:

$$K_{x(3)} = \frac{[m(\mathrm{CO})]^2}{m(\mathrm{CO})_2 \sum m_i},$$

$$K_{x(4)} = \frac{m(\mathrm{CO})\,[m(\mathrm{H_2})]^3}{m(\mathrm{CH_4})\,m(\mathrm{H_2})\,(\sum m_i)^2}$$

$$K_{x(6)} = \frac{m(\mathrm{CO_2})\,m(\mathrm{H_2})}{m(\mathrm{CO})\,m(\mathrm{H_2O})}$$

$$2m_0(\mathrm{CH_4}) + m_0(\mathrm{H_2O}) = m(\mathrm{H_2}) + 2m(\mathrm{CH_4}) + m(\mathrm{H_2O})$$

$$m_0(\mathrm{H_2O}) + m_0(\mathrm{CO}) + 2m_0(\mathrm{CO_2}) = m(\mathrm{H_2O}) + m(\mathrm{CO}) + 2m(\mathrm{CO_2})$$

The equilibrium constants can be calculated by approximate equations holding for the temperature interval 800-1200 K (the equation for $\log K_{x(3)}$ is given above):

$$\log K_{x(4)} = 2\log\left(\frac{p^\circ}{p}\right) + 11.20 - \frac{10\,680}{T}$$

$$\log K_{x(6)} = -1.98 + \frac{2120}{T}$$

Assume, for example, that methane is being converted at 1000 K, at standard pressure ($p = p^\circ$), and the initial mixture contains two moles of H_2O [$m_0(H_2O) = 2$] per mole of methane [$m_0(CH_4) = 1$]. Hence, taking into account the expressions for K_x, we obtain the following system of equations:

$$0.3 = \frac{m(\mathrm{CO})\,[m(\mathrm{H_2})]^3}{m(\mathrm{CH_4})\,m(\mathrm{H_2O})\,(\sum m_i)^2}$$

$$1.4 = \frac{m(\mathrm{CO_2})\,m(\mathrm{H_2})}{m(\mathrm{CO})\,m(\mathrm{H_2O})}$$

Let us supplement the system with five unknown m_i's by adding three equations of the hydrogen, oxygen, and carbon atom balances (the equality of the number of atoms in the feed stock and equilibrium mixture):

$$8 = 2m(\mathrm{H_2}) + 4m(\mathrm{CH_4}) + 2m(\mathrm{H_2O}) \quad \text{(H atom balance)}$$

$$2 = m(\mathrm{CO}) + m(\mathrm{H_2O}) + 2m(\mathrm{CO_2}) \quad \text{(O atom balance)}$$

$$1 = m(\mathrm{CO}) + m(\mathrm{CH_4}) + m(\mathrm{CO_2}) \quad \text{(C atom balance)}$$

The use of the search gradient method (Newton-Raphson) for this system gives $m(H_2O) \approx 1.2$, $m(CO) = 0.3$, $m(CH_4) = 0.45$, $m(CO_2) = 0.25$, and $m(H_2) = 1.9$.

The performance of such calculations (see also Sec. 3.5) for each specific case involves no difficulties when the standard search programmes for computers treated in Chap. 3 are employed. For exam-

ple, at atmospheric pressure and a molar ratio of CH_4:H_2O = 1, the content of the components in an equilibrium mixture is as follows [63, 64]:

Components	CH_4	CO_2	CO	H_2
Content, % (mol.):				
at 826 °C	0.1	4.7	19.1	76.1
at 924 °C	—	3.8	20.3	73.9

If only reaction (4) would proceed, the equilibrium mixture at 826 °C would contain 2.9% of CH_4, 23.4% of CO, and 70% of H_2, i.e. a transition to a simple reaction at high temperatures lowers the possible formation of hydrogen by about 6%.

If it is necessary to obtain only hydrogen, then from the standpoints of thermodynamic analysis it is good practice to perform conversion in two steps, namely, at high temperatures (above 700 °C) reaction (6), and at moderate ones (400-500 °C), reaction (4).

8.2. Syntheses of Oxygen-Containing Compounds Based on CO and H

8.2.1. Production of Methanol

The synthesis of methanol from CO and H_2 is an important industrial process. The use of copper-containing catalysts instead of zinc-chromium ones made it possible to lower the pressure from 25-35 MPa to 5-10 [61].

Thermodynamically, the synthesis of methanol from CO or CO_2 by the following exothermic reactions is possible:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^\circ = -91.9\ \text{kJ} \qquad \text{(a)}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^\circ = -49.5\ \text{kJ} \qquad \text{(b)}$$

It is obvious that reaction (a) can be obtained by combining reaction (b) and the water gas reaction

$$CO + H_2O \rightarrow CO_2 + H_2, \qquad \Delta H^\circ = -42.4\ \text{kJ} \qquad \text{(c)}$$

i.e. (a) = (b) + (c).

The temperature dependence of K_p° for the synthesis of methanol by reaction (a) was first proposed by Temkin and Cherednichenko [4, 63] in the form

$$\log K_{p(a)}^\circ = \frac{3971}{T} - 7.492 \log T + 0.001\,77T - 0.311 \times 10^{-7}T^2 + 9.218$$

The use of more up-to-date thermodynamic data results in the equation [61]:

$$\log K_{f(a)}^\circ = \frac{3921}{T} - 7.971 \log T + 2.5 \times 10^{-3}T - 2.953 \times 10^{-7}T^2 + 10.2 \qquad (8.1)$$

The difference between the values of K_p° calculated by these equations is not great.

Information on other equations is contained in [4, 65]. The value of K_p° for reaction (b) can be calculated from $K_{p(a)}^\circ$ and the equilibrium constant of the water gas reaction $K_{p(c)}^\circ$:

$$K_{p(a)}^\circ = K_{p(b)}^\circ K_{p(c)}^\circ \text{ or}$$

$$K_{p(b)}^\circ = \frac{K_{p(a)}^\circ}{K_{p(c)}^\circ}$$

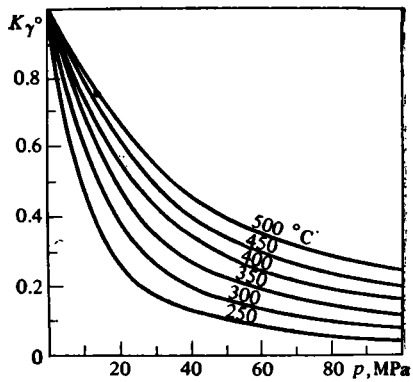


Fig. 38. Dependence of K_γ° for the synthesis of methanol by the reaction $CO + 2H_2 \rightarrow CH_3OH$ on the pressure and temperature

The values of $K_{p(c)}^\circ$ are given in Sec. 8.1. Since methanol is synthesized at increased pressure, the non-ideal nature of the system has to be taken into account for calculating the equilibrium compositions. To go over to the real equilibrium constants, we can use a plot of K_γ° for reaction (a) against the temperature and pressure (Fig. 38).

For illustration, we shall present data [4, 65] on the equilibrium conversion of CO to methanol at various temperatures and pressures for industrial synthesis gas containing [in % (mol.)]: CO_2—4, CO—26, H_2—60, and inert impurities—10 (see also Fig. 39):

Temperature, °C	260	300	340	380	420
Equilibrium degree of conversion of CO, % (mol.):					
at 5 MPa	46	18	4	<1	<1
at 10 MPa	72	44	18	4	<1
at 30 MPa	90	79	65	50	38

A glance at the above data reveals that the process will be effective at low temperatures and high pressures. If the catalyst is active enough to conduct the process at temperatures of about 260 °C, then synthesis can be performed at 5-10 MPa (we call this **low-pressure synthesis**); for less active catalysts functioning effectively at 400 °C, the use of high pressures (about 30 MPa) is required. Since the degree of conversion is substantially below 100% under all conditions, recirculation has to be resorted to.

Pressures exceeding 30-35 MPa are not used in industrial processes owing to the increase in the rate of side reactions such as the formation of methane, dimethyl ether, and higher alcohols. The degree of conversion of CO in the low-pressure processes during one pass ranges from 15 to 50%, while in high-pressure processes it does not exceed 25%.

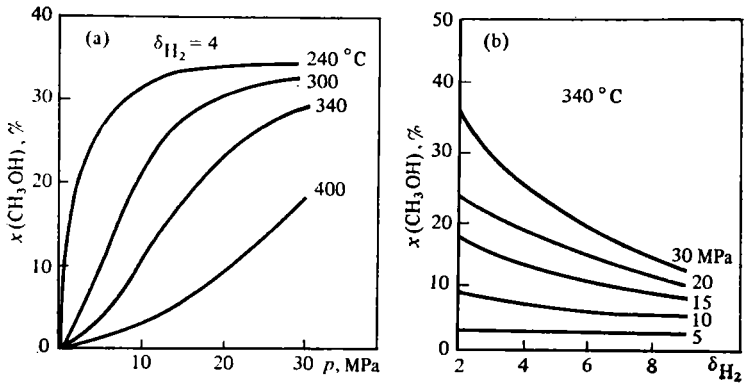


Fig. 39. Methanol content in an equilibrium gas mixture for the reaction $CO + 2H_2 \rightarrow CH_3OH$ at various temperatures (*a*), pressures and molar ratios δ_{H_2} (H_2:CO) in the initial mixture (*b*)

A comparison of these data with the thermodynamically equilibrium values given above shows that the indices of the process can be improved.

As regards reaction (b), its thermodynamic probability is considerably lower than that of reaction (a); the equilibrium degree of conversion, for example, at 260 °C for the mixture indicated above is 4% at 5 MPa, 6% at 10 MPa, and 13% at 30 MPa.

8.2.2. Production of Higher Alcohols

Alcohols with a higher molecular mass are also synthesized from CO and H_2. The introduction of a small amount of an alkali (about 1%) into the methanol synthesis catalyst made it possible to produce appreciable amounts of isobutanol together with the methanol. The liquid products contained about 50% (mass) methanol, 14% isobutanol, and 8% C_5-C_8 alcohols.

Ethylene glycol was produced in the presence of cobalt-, manganese-, chromium- or rhodium-containing catalysts at 150-400 °C and pressures above 150 MPa.

A mixture of aliphatic alcohols was produced from CO and H_2 at 200 °C and 2 MPa in the presence of a hydrogenating iron catalyst—the synol process. The introduction of cerium or vanadium into these catalysts and the precipitation of the active components on the carrier made it possible to increase the yield of alcohols—the oxyl process. Its products contain 55% of alcohols, including 10% of ethyl, 7% of propyl, 6% of butyl, 4-5% each of amyl and hexyl alcohols, and 5-7% each of mixtures of C_7-C_8, C_9-C_{10}, C_{11}-C_{12}, and C_{13}-C_{18} alcohols. Table 103 presents the heats and equilibrium constants of the synthesis of alcohols with two or more carbon atoms from CO and H_2.

The data in Table 103 relate to the production of primary normal alcohols. The reactions can be seen to be exothermic, namely, from 130 to 145 kJ are evolved per mole of carbon in a formed alcohol. The reactions proceed practically to the end at low (300-400 K) temperatures, but at higher ones the thermodynamic restrictions are very significant. Thus, for log $K_p^\circ = -1.74$ (for the preparation of ethanol at 600 K), the degree of conversion of CO at atmospheric pressure is below 10%. The degree of conversion is also increased by raising the pressure. The most favourable H_2:CO ratio in synthesis gas is two.

Table 103. **Heats ΔH° (in kJ) and Equilibrium Constants K_p° of Synthesis of C_2 and Higher Alcohols from CO and H_2**

Reaction	Temperature, K			
	300		600	
	$-\Delta H^\circ$	$\log K_p^\circ$	$-\Delta H^\circ$	$\log K_p^\circ$
$2CO+4H_2 \rightarrow C_2H_5OH+H_2O$	255.6	21.2	271.8	−1.74
$3CO+6H_2 \rightarrow C_3H_7OH+2H_2O$	409.7	36.1	432.2	−0.53
$4CO+8H_2 \rightarrow C_4H_9OH+3H_2O$	553.5	49.8	587.9	0.04
$5CO+10H_2 \rightarrow C_5H_{11}OH+4H_2O$	717.1	65.3	753.5	1.53

A thermodynamic analysis of the oxyl process allows us to explain the predominating formation of secondary and especially of tertiary alcohols at elevated temperatures. For these alcohols, log $K_{p,f}^\circ$ is higher than for the primary ones, and therefore the equilibrium constants for their synthesis from CO and H_2 are considerably higher than for normal primary alcohols. Thus, for 600 K, the value of log K_p° for the production of secondary propanol is 0.04, of secondary butanol is +1.37, and of tertiary butanol is +2.60, i.e. K_p° for the synthesis of secondary and tertiary alcohols is one or two orders of magnitude higher than that for the synthesis of primary ones. This is exactly what explains the formation of tertiary (and not primary) butanol as a side product in the synthesis of methanol.

8.2.3. Production of Aldehydes and Alcohols by Reacting Alkenes with Synthesis Gas (Oxo Process)

Almost all the alkenes enter into the reactions of the oxo process:

$$R{-}CH{=}CH_2+CO+H_2 \rightarrow R{-}CH_2{-}CH_2{-}CHO,$$
$$R{-}CH{=}CH_2+CO+2H_2 \rightarrow R{-}CH_2{-}CH_2{-}CH_2OH$$

The process is conducted for ethylene in the gas phase. For alkenes with three or more carbon atoms, the phase state of the alkene and

Table 104. **Heats ΔH° (in kJ) and Equilibrium Constants K_p° for Reactions of C_2-C_4 Alkenes**

Reaction (reactants in state of ideal gas)	Temperature, K							
	300		400		500		600	
	$-\Delta H^\circ$	$\log K_p^\circ$	$-\Delta H^\circ$	$\log K_p^\circ$	$-\Delta H^\circ$	$\log K_p^\circ$	$-\Delta H^\circ$	$\log K_p^\circ$
$C_2H_4 + CO + H_2 \rightarrow C_2H_5CHO$	134.1	10.6	136.0	4.7	136.5	0.9	138.0	—1.2
$C_3H_6 + CO + H_2 \rightarrow C_3H_7CHO$	115.1	7.8	116.7	1.9	117.6	—1.2	118	—3.2
$C_3H_6 + CO + H_2 \rightarrow (CH_3)_2CHCHO$	127.0	8.1	129.0	2.2	130.0	—0.9	132	—2.8
$C_4H_8 + CO + H_2 \rightarrow C_4H_9CHO$	117.0	7.3	119.7	2.1	120.0	—1.0	120	—3.1
$C_4H_8 + CO + H_2 \rightarrow C_2H_5CH(CH_3)CHO$	129.5	7.8	131.0	2.4	133.0	—0.8	132	—2 9

the aldehyde or alcohol can be either a gas or liquid. Liquid-phase processes are the most widespread. They are carried out in the presence of catalysts—metal carbonyls at temperatures of about 100 °C and pressures up to 30 MPa, chiefly 10-15 MPa. At a $CO:H_2$ molar ratio in the synthesis gas equal to unity, isomer aldehydes form. For example, two isomer aldehydes are produced from propylene:

$$C_3H_6 + CO + H_2 \rightarrow CH_3—CH_2—CH_2—CHO,$$

$$C_3H_6 + CO + H_2 \rightarrow CH_3—\underset{\underset{CH_3}{|}}{CH}—CHO$$

If synthesis gas with a high hydrogen content is used, hydrogenation of the aldehydes can be performed, and the products of the oxo reaction will be alcohols. However, both from thermodynamic and, especially, from technological considerations, the step of producing aldehydes is separated from that of their hydrogenation into alcohols.

The thermodynamics of the oxo process reactions has been considered for gas phase reactions; in early publications, the estimates of K_p° differed by two orders of magnitude [34]. In this connection, Table 104 gives the values of the heats and equilibrium constants for reactions of alkenes with two to four carbon atoms having an industrial significance.

The values of ΔH° are close to those determined earlier; the values of K_p° found by us are appreciably lower than the published ones [4, 34], and, since the latter are based on obsolete determinations, they should not be used.

Inspection of the above data shows that the temperature greatly affects oxo process reactions. At 300 K, these reactions proceed like virtually irreversible ones. For 400 K, the value of K_p° has the order of magnitude of 10^2, and at 500 K, already 10^{-1} (for reactions of alkenes with three or more carbon atoms). Let us assess, at these values of K_p° and two compositions of the gas mixture, the equilibrium degrees of conversion of an alkene y (fractions). Presuming that the reaction proceeds in an ideal gas phase, we obtain the following equation relating K_p°, y, the standard and real pressures (p° and p), and the molar ratios CO:alkene [δ(CO)] and H_2:alkene [$\delta(H_2)$] in the initial mixture:

$$K_p^\circ \left(\frac{p}{p^\circ}\right)^2 \quad K_x = \frac{y\,[1+\delta(CO)+\delta(H_2)-2y]^2}{(1-y)\,[\delta(CO)-y]\,[\delta(H_2)-y]} \qquad (8.2)$$

The values of y obtained by calculations using Eq. (8.2) are given in Table 105.

It can be seen from Table 105 that at temperatures up to 450 K (used in the industry) practically complete conversion of an alkene can be achieved by employing high pressures and dilution of the alkene with synthesis gas. At higher temperatures, the thermodynam-

ic restrictions become substantial. This is why the degrees of conversion of an alkene of 60-70% obtained under industrial conditions for a gas-phase process are close to the equilibrium ones.

Calculations for a real gas mixture will insignificantly increase the estimates of the degree of conversion given in Table 105 because K_{γ° is close to 0.9 (the specific calculations have been omitted), and for a reaction in a real gas mixture K_x is larger than the values given in Table 105 by about 10%. It is obvious, however, that such an insignificant change in K_x will increase the equilibrium degree of conversion of an alkene by not over 1-2%.

Table 105. **Equilibrium Degrees of Conversion of Alkenes at Various Temperatures and Pressures**

Temperature, K	Pressure, MPa	K_x	Equilibrium degree of conversion of alkene y (fractions) at $\delta(CO) = \delta(H_2)$	
			1	2
400	0.1	10^2	0.75	0.95
	10	10^4	0.9	0.99
	30	3×10^4	0.98	0.99
425	0.1	13.1	0.5	0.65
	10	1310	0.9	0.99
	30	3930	0.93	0.99
450	0.1	2.1	0.15	0.2
	10	210	0.8	0.95
	30	630	0.86	0.99
475	0.1	0.4	0.05	0.06
	10	40	0.6	0.8
	30	120	0.75	0.9
500	0.1	0.1	0.01	0.02
	10	10	0.4	0.6
	30	30	0.6	0.8

Equilibrium for a gas-liquid system (the alkene and aldehyde are liquid, while the CO and H_2 are gaseous) can be calculated by the methods described in Chap. 2. In each specific case, special calculations are needed for which information is required on the solubility of the gases in the liquid, the fugacities of the components, etc.

For this reason, below we shall limit ourselves to a treatment of the case when the solution can be considered ideal, the vapour pressure of the liquid component over the solution obeys Raoult's law, while the solubility of the gas obeys Henry's law. Even in this case, the calculation of the equilibrium of the gas-liquid reaction from the equilibrium of the reaction in the gas phase (see Chap. 2) is hindered by the absence or lack of reliability of the data on the solubility of H_2 and CO in the liquid phase containing the alkene, alde-

hyde, and catalyst. It is not difficult, however, to obtain an expression indicating the nature of the change in the composition of the gas-liquid reaction (x_i^{lq} is the mole fraction of substance i in the liquid) in comparison with the composition of the gas-phase reaction (x_i is the mole fraction of substance i in the equilibrium gas phase). It is easy to find the values of x_i from the equilibrium degree of conversion of the alkene y given above:

$$x\,(\mathrm{R'CH=CH_2}) = \frac{1-y}{1+\delta\,(\mathrm{CO})+\delta\,(\mathrm{H_2})-2y},$$

$$x\,(\mathrm{RCHO}) = \frac{y}{1+\delta\,(\mathrm{CO})+\delta\,(\mathrm{H_2})-2y}$$

If p_i° is the saturated vapour pressure of component i, then for an approximate estimate of the composition of the gas-liquid mixture (the pressure for the gas-liquid reaction for which the calculations are being performed must be established additionally), we can consider that

$$\frac{x\,(\mathrm{RCHO})^{lq}}{x\,(\mathrm{R'CH=CH_2})^{lq}} = \frac{x\,(\mathrm{RCHO})}{x\,(\mathrm{R'CH=CH_2})}\,\frac{p^\circ\,(\mathrm{R'CH=CH_2})}{p^\circ\,(\mathrm{RCHO})}$$

The ratio $p^\circ(\mathrm{R'CH=CH_2})/p^\circ(\mathrm{RCHO})$ depends on the temperature, but is generally large. Therefore, even with low degrees of conversion for the gas-phase reaction, the reaction in the gas-liquid system can proceed with high degrees of conversion. For example, at $y = 0.1$ and $p^\circ(\mathrm{R'CH=CH_2})/p^\circ(\mathrm{RCHO}) = 10$, we have $x(\mathrm{RCHO})^{lq}/x(\mathrm{R'CH=CH_2})^{lq} = 1$ and $y^{lq} = 0.5$, while when $p^\circ(\mathrm{R'CH=CH_2})/p^\circ(\mathrm{RCHO}) = 100$, we have $x(\mathrm{RCHO})^{lq}/x(\mathrm{R'CH=CH_2})^{lq} = 10$, and $y^{lq} = 0.91$.

It can be concluded that the conducting of the reaction in a gas-liquid system at temperatures up to 500 K and pressures above 10 MPa is possible with degrees of conversion of the alkene approaching 100%.

The thermodynamic analysis of an oxo reaction with the direct production of an alcohol is of no interest because under industrial conditions the steps of aldehyde production and its hydrogenation into an alcohol are separated. In this connection, we shall characterize the reaction of hydrogenation of aldehydes with three or more carbon atoms into the relevant alcohols.

The hydrogenation of aldehydes proceeds with the evolution of heat. The heat of a reaction conducted in the gas phase is about −70 kJ/mol at 300 K and −75 kJ/mol at 600 K. The hydrogenation equilibrium constant K_p° at temperatures of 300, 400, 500, and 600 K is $10^{6.2}$, $10^{3.2}$, $10^{1.3}$, and 10^0, respectively, so that for the temperature interval 300-600 K we have:

$$\log K_p^\circ = -6.2 + \frac{3720}{T}$$

This shows that the hydrogenation of an aldehyde can be performed up to the following equilibrium degrees of conversion y_1 of it:

Temperature, K . .	300-400		500		600	
Pressure, MPa . . .	0.1 and above	0.1	10 and above	0.1	10	10
Hydrogen:aldehyde ratio	1 and above	1	1 and above	1	1	10
y_1, fractions	≈1	0.8	≈1	0.4	0.9	0.99

A glance at these data reveals that the hydrogenation of aldehydes can be conducted practically to the end even at 600 K by increasing the pressure and the supply of hydrogen.

8.3. Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen

The synthesis of hydrocarbons from a mixture of $CO + H_2$ (Fischer-Tropsch synthesis) is conducted in the presence of microheterogeneous metallic (Ni, Co, Fe, Ru, etc.) or solid (a metal on an alumina carrier) catalysts at temperatures of 150-500 °C and pressures of 0.1-100 MPa.

The formation of hydrocarbons proceeds with the evolution of water or CO_2, for example, alkanes form by the reactions

$$(2n+1)\,H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \quad (1)$$

$$(n+1)\,H_2 + 2nCO \rightarrow C_nH_{2n+2} + nCO_2 \quad (2)$$

These reactions are attended by the evolution of heat (Table 106).

The considerable evolution of heat (up to 25% of the heat of combustion of synthesis gas) results in difficulties when realizing the process on an industrial scale. It is also obvious that it is expedient to attempt to obtain an equation enabling one to calculate $\Delta H°$ for the Fischer-Tropsch synthesis for a hydrocarbon of the given structure and for an arbitrary temperature. A number of investigators have drawn attention to the circumstance that for hydrocarbons of one kind and at a constant temperature, the value of $\Delta H°/n$, i.e. the heat of obtaining of a hydrocarbon related to one mole of carbon in the hydrocarbon, is independent of n (see [63]). The relations $\Delta H_f^\circ = f(T, n)$ given in Appendix 1 enable one to explain this and obtain $\Delta H°$ as a function of T and n.

Let us consider the reactions of synthesis of alkanes. For these reactions, we have:

$$\Delta H° = [\Delta H_f^\circ(C_nH_{2n+2}) + n\Delta H_f^\circ(H_2O)] - n\Delta H_f^\circ(CO) \text{ [reaction (1)]}$$

$$\Delta H° = [\Delta H_f^\circ(C_nH_{2n+2}) + n\Delta H_f^\circ(CO_2)] - 2n\Delta H_f^\circ(CO) \text{ [reaction (2)]}$$

We have shown that $\Delta H_f^\circ/n$ depends only slightly on n.

Treatment of the data reveals that for temperatures of 200-500 °C for type (1) reactions we can assume the following:

$\Delta H^\circ/n = -159$ kJ/mol of carbon in the synthesis of alkanes and cycloalkanes ($n \geqslant 6$);

$\Delta H^\circ/n = -155$ kJ/mol of carbon in the synthesis of alkenes ($n \geqslant 8$);

$\Delta H^\circ/n = -127$ kJ/mol of carbon in the synthesis of aromatics ($n \geqslant 6$).

An estimate of the values of ΔH° using these relations yields results sufficiently close to values given in Table 106 for 400 or 700 K. The discrepancy for ΔH° does not exceed 4%.

Table 106. **Heats of Hydrocarbon Synthesis after Fischer-Tropsch**

Hydrocarbon formed	Heat of reaction $-\Delta H^\circ$, kJ/mol			
	(1)		(2)	
	400 K	700 K	400 K	700 K
Alkane				
CH_4	210.7	220.5	251.0	258.4
C_2H_6	355.1	370.6	436.3	446.4
C_3H_8	508.5	528.8	630.4	642.5
C_4H_{10}	663.3	688.2	825.8	839.7
C_6H_{14}	973.7	1008.2	1217.5	1235.5
C_8H_{18}	1283.0	1326.7	1608.0	1629.7
$C_{10}H_{22}$	1592.1	1645.5	2013.4	2024.2
$C_{20}H_{42}$	3138.0	3238.8	3950.2	3996.1
Alkene				
C_2H_4	216.2	227.9	297.5	303.6
C_3H_6	382.5	400.0	504.4	513.6
C_4H_8	535.5	556.9	697.9	708.3
C_8H_{16}	1155.6	1195.8	1480.7	1498.7
$C_{20}H_{40}$	3010.4	3107.5	3822.9	3865.2
Cycloalkane				
C_6H_{12}	920.5	964.0	1172.8	1191.2
$C_6H_{11}—CH_3$	1095.4	1132.2	1379.9	1397.5
Aromatic				
C_6H_6	718.8	743.9	962.7	971.1
$C_6H_5—CH_3$	885.7	916.3	1170.3	1181.6
Acetylene				
C_2H_2	38.9	45.2	120.1	120.9
$C_2H—CH_3$	215.1	228.0	336.8	341.4

The heats of type (2) reactions can be obtained on the basis of those of type (1) reactions. To do this, we must have in view that a type (2) reaction can be obtained by combining a type (1) reaction and n reactions of water gas ($CO + H_2O \rightarrow CO_2 + H_2$). Hence, the heat of reaction (2) with the obtaining of an alkane C_nH_{2n+2} equals the sum of the heats of reactions (1) (with the obtaining of the same alkane) and n heats of the water gas reactions ($\Delta H^\circ_{w.g} = -40$ kJ). As a result, we can assume the following for type (2) reactions:

$\Delta H^\circ/n = -199$ kJ/mol of carbon in the synthesis of alkanes and cycloalkanes ($n \geqslant 6$);

$\Delta H^\circ/n = -195$ kJ/mol of carbon in the synthesis of alkenes ($n \geqslant 8$);

$\Delta H^\circ/n = -167$ kJ/mol of carbon in the synthesis of aromatics ($n \geqslant 6$).

A comparison of the above data shows that for reactions (2) the discrepancies between the estimates and accurate values of ΔH° for temperatures of 400-800 K also do not exceed 4%.

Let us now consider the data on the equilibrium constants of the hydrocarbon synthesis reactions after Fischer and Tropsch (Table 107).

Table 107. **Logarithms of the Standard Equilibrium Constants of Reactions (1) and (2) of Hydrocarbon Synthesis After Fischer and Tropsch**

Hydrocarbon formed	log K_p° at T, K							
	300		500		700		900	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Alkane								
CH_4	24.7	29.6	10.1	12.1	3.6	4.5	—0.1	1.2
C_2H_6	37.4	47.3	12.7	17.0	1.8	3.7	—4.4	3.6
C_6H_{14}	94.9	124.6	27.4	40.1	—2.4	3.3	—12.1	—17.2
$C_{10}H_{22}$	152.3	201.8	41.8	63.0	—6.9	2.7	—34.2	—30.8
$C_{20}H_{42}$	295.6	394.7	77.8	120.2	—18.0	1.1	—71.9	—65.0
Alkene								
C_2H_4	19.8	29.7	4.8	9.1	—1.8	0.1	—5.6	—5.0
C_8H_{16}	108.5	144.3	28.3	45.3	—7.0	0.6	—26.9	—24.2
$C_{20}H_{40}$	280.6	379.6	71.6	114.0	—20.4	—1.3	—72.1	—65.2
Cycloalkane								
C_6H_{12}	89.5	119.2	24.9	37.6	—3.6	2.1	—19.7	—17.6
C_6H_{11}—CH_3	106.1	140.7	30.0	44.9	—3.5	3.2	—22.3	—19.9
Aromatic								
C_6H_6	72.6	102.2	22.6	35.4	0.7	6.4	—11.7	—9.7
C_6H_5—CH_3	89.6	124.3	28.1	43.0	1.1	7.7	—14.2	—11.8

Examination of the data of Table 107 reveals that elevation of the temperature is attended by lowering of the thermodynamic probability of the synthesis, but for all the hydrocarbons it remains sufficiently high up to about 800 K. Synthesis after Fischer and Tropsch is also possible, true, with low degrees of conversion, at a temperature about 1100 K. The somewhat higher thermodynamic probability of synthesis by reaction (2), and also the differences in the probabilities of forming hydrocarbons of various types are of no significance because the selectivity of the process is determined not by thermodynamic, but by kinetic factors.

Attempts are sometimes made in the literature to present the temperature dependence of ΔG° and K_p° in the form of a linear one, which is not consistent with the relations of thermodynamics. With a view to the only slight temperature dependence of ΔH°, we can substantiate the following equation:

$$\log K_p^\circ = a + \frac{b}{T} \tag{8.3}$$

that will hold for every reaction. At the same time, it can be seen from the data of Table 107 that the following conditions are observed for $\log K_p^\circ$ and also for ΔG° for the synthesis of hydrocarbons of one group:

$$\frac{\Delta G^\circ}{n} \neq f(n), \quad \frac{\log K_p^\circ}{n} \neq \varphi(n)$$

It is therefore convenient to generalize $\log K_p^\circ$ as a function of $1/T$ for the hydrocarbons of one group. A treatment of the data of Table 107 yields the following expressions for calculating K_p° for reactions of type (1):

$\log K_p^\circ/n \approx 8.2 \times 10^3/T - 12$ for the synthesis of alkanes and cycloalkanes ($n \geqslant 6$);

$\log K_p^\circ/n = 7.7 \times 10^3/T - 12.4$ for the synthesis of alkenes ($n \geqslant 8$).

$\log K_p^\circ/n = 7.7 \times 10^3/T - 14$ for the synthesis of aromatics ($n \geqslant 6$).

To calculate K_p° for type (2) reactions, one must have in view that $\log K_p^\circ/n$ for these reactions can be obtained by summing $\log K_p^\circ/n$ for type (1) reactions and $\log K_p^\circ$ for the synthesis of water gas because the sum of the reactions

$$2H_2 + CO \rightarrow [-CH_2-] + H_2O \quad \text{[reaction (1)]}$$

and

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{(reaction of water gas)}$$

yields

$$H_2 + 2CO \rightarrow [-CH_2-] + CO_2 \quad \text{[reaction (2)]}$$

The use of the accurate values of $\log K_p^\circ$ for the water gas reaction gives sufficiently good agreement of the calculated and experimental values of $\log K_p^\circ$ for reactions (2). To estimate $\log K_p^\circ$ for reactions (2), we can assume that for the temperature interval 400-800 K, the value of $\log K_p^\circ$ for the water gas reaction is about 1.2. Hence, for type (2) reactions, we have

$$\left(\frac{\log K_p^\circ}{n}\right)_{(2)} \approx \left(\frac{\log K_p^\circ}{n}\right)_{(1)} + 1.2 \tag{8.4}$$

One must bear in mind, however, that expression (8.4) is less accurate in comparison with the expressions for a type (1) reaction.

When calculating equilibrium compositions, generally speaking, one must take into consideration the non-ideal nature of the system.

But for the moderate pressures generally employed for synthesis (up to 5 MPa), the fugacities of the components are close to their partial pressures, and the assumption that the system is ideal introduces no appreciable error into the calculations.

Assume that we have determined the equilibrium constant K_p° of reaction (1)

$$K_p^\circ = K_p\,(p^\circ)^{2n} = K_x\left(\frac{p^\circ}{p}\right)^{2n}$$

where $K_x = x(C_nH_{2n+2})[x(H_2O)]^n/[x(H_2)]^{2n+1}[x(CO)]^n$, p° is the standard pressure (101 325 Pa), and p is the pressure at which the reaction is conducted.

Having determined the constant K_x from K_p°, we can further find the equilibrium degree of conversion y of one of the reactants, for example, CO. Designating the molar ratio H_2:CO in the initial mixture by δ, we obtain an equation for finding y (see Sec. 1.7):

$$K_x = \frac{(y/n)\,y^n\,(1+\delta-2y)^{2n}}{\left(\delta-\dfrac{2n+1}{n}\,y\right)^{2n+1}(1-y)^n} \tag{8.5}$$

If we use the stoichiometric ratio of the reactants, then $\delta = (2n+1)/n$, and hence

$$K_x = \frac{y^{n+1}\left(\dfrac{3n+1}{n}-2y\right)^{2n}}{n\left(\dfrac{2n+1}{n}\right)^{2n+1}(1-y)^{3n+1}} \tag{8.6}$$

For example, for the production of decane ($n = 10$)

$$K_x = \frac{y^{11}\,(3.1-2y)^{20}}{10\,(21/10)^{21}\,(1-y)^{31}}$$

In this case, the value of $K_x = 1 \times 10^{25}$ corresponds to $y = 0.9$, and $K_x = 8 \times 10^{-7}$ to $y = 0.1$. These calculations reveal that both very large and very small values of the equilibrium constants give no grounds for conclusions on the irreversibility of the reactions.

Thermodynamic Analysis of Fischer-Tropsch Multistep Synthesis of Hydrocarbons. In the thermodynamic analysis of the synthesis of hydrocarbons varying in their molecular mass, one can use a scheme with a gradually increasing number of carbon atoms:

$$3H_2 + CO \xrightarrow{1} CH_4 + H_2O$$

$$2H_2 + CO + CH_4 \xrightarrow{2} C_2H_6 + H_2O$$

$$\cdots\cdots\cdots\cdots \qquad \cdots\cdots$$

$$2H_2 + CO + C_{n-1}H_{2(n-1)+2} \xrightarrow{n} C_nH_{2n+2} + H_2O$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

The overall rate of hydrocarbon formation is

$$w_f = k_f\,[p\,(H_2)]^2\,p\,(CO)\sum p\,(C_nH_{2n+2})$$

while the rate of their decomposition is

$$w_{dec} = k_{dec}p\,(H_2O)\sum p\,(C_nH_{2n+2})$$

In equilibrium, $w_f = w_{dec}$ and, therefore,

$$K_p = \frac{k_f}{k_{dec}} = \frac{p(H_2O)}{[p(H_2)]^2 p(CO)} \tag{8.7}$$

Here K_p is the equilibrium constant of hydrocarbon synthesis.

If $n \geqslant 6$, then as has been shown above, the equilibrium constant for each step of the scheme is the same. Consequently, K_p in the last equation is calculated by conventional thermodynamic methods.

Equation (8.7) enables us to determine the overall degree of conversion of the reactants into hydrocarbons. This equation presumes that the reaction

$$2H_2 + CO \rightarrow [-CH_2-] + H_2O$$

proceeds. If, as previously, we let δ stand for the molar ratio H_2:CO in the initial mixture, and y for the degree of conversion of the CO, we have

$$K_x = K_p^\circ \left(\frac{p}{p^\circ}\right)^2 = \frac{y\,(1+\delta-y)}{(\delta-2y)^2\,(1-y)} \tag{8.8}$$

Equation (8.8) is convenient for estimating the total possible degree of conversion in the synthesis of hydrocarbons. For example, for the synthesis of alkanes and cycloalkanes we find that for 600 K the standard equilibrium constant is $K_p^\circ = 46.4$. If $p = p^\circ = 101\,325$ Pa and $\delta = 2$, then from Eq. (8.8) we find that $y = 0.8$. If, on the other hand, $p/p^\circ = 50$, then the equilibrium degree of conversion of CO of hydrocarbons will be close to 0.95. In other words, virtually complete conversion of one of the reactants can be obtained by employing moderate temperatures and high pressures. At relatively low temperatures ($\leqslant$500 K), virtually complete conversion can also be achieved at atmospheric pressure. It should be stressed that Eq. (8.8) and calculations take into account the conversion of CO and H_2 into all the hydrocarbons formed.

To analyse the thermodynamic probability of the formation of hydrocarbons of a various molecular mass, let us consider the expressions for the equilibrium constants K_c of the steps; it is simple to obtain them from the constants K_p:

$$K_{c,i} = K_{p,i}\,(RT)^{-\Sigma\nu_i} \tag{8.9}$$

For the separate steps of the scheme, Eq. (8.9) acquires the following expressions:

step 1:

$$3H_2 + CO \rightarrow CH_4 + H_2O$$

$$K_{c,1} = \frac{c(CH_4)\,c(H_2O)}{[c(H_2)]^3\,c(CO)} \quad \text{or} \quad c(CH_4) = K_{c,1}c(H_2)\,a$$

where

$$a = \frac{[c(H_2)]^2\,c(CO)}{c(H_2O)}$$

step 2:

$$2H_2 + CO + CH_4 \rightarrow C_2H_6 + H_2O$$

$$K_{c,2} = \frac{c(C_2H_6)}{c(CH_4)\,a}$$

or

$$c(C_2H_6) = K_{c,2}\,c(CH_4)\,a = K_{c,2}K_{c,1}\,c(H_2)\,a^2$$

step n:

$$2H_2 + CO + C_{n-1}H_{2(n-1)+2} \rightarrow C_nH_{2n+2} + H_2O$$

$$K_{c,n} = \frac{c(C_nH_{2n+2})}{c[C_{n-1}H_{2(n-1)+2}]\,a}$$

or

$$c(C_nH_{2n+2}) = K_{c,n} \ldots K_{c,2}K_{c,1}c(H_2)\,a^n$$

The total concentration of hydrocarbon molecules c_h is determined by the following equation:

$$c_h = c(CH_4) + c(C_2H_6) + \ldots + c(C_nH_{2n+2}) + \ldots$$
$$= K_{c,1}\,c(H_2)\,a\,(1 + K_{c,2}a + \ldots + K_{c,n} \ldots K_{c,2}a^{n-1}) \qquad (8.10)$$

Let us now determine the number of carbon atoms L in the hydrocarbon molecules:

$$L = \sum_i n_i c_i = 1c(CH_4) + 2c(C_2H_6) + \ldots + nc(C_nH_{2n+2})$$
$$= K_{c,1}c(H_2)\,a\,(1 + 2K_{c,2}a + \ldots + nK_{c,n} \ldots K_{c,2}a^{n-1})$$

The ratio of L to c_h determines the mean number $\bar{n}$ of carbon atoms in a molecule of the hydrocarbon being synthesized. Hence:

$$\bar{n} = \frac{L}{c_h} = \frac{1 + 2K_{c,2}a + \ldots + nK_{c,n}K_{c,n-1} \ldots K_{c,2}a^{n-1}}{1 + K_{c,2}a + \ldots + K_{c,n}K_{c,n-1} \ldots K_{c,2}a^{n-1}} \qquad (8.11)$$

If all the equilibrium constants are the same, for example, $K_{c,2} = K_{c,3} = \ldots = K_c$, Eq. (8.11) becomes

$$\bar{n} = \frac{1 + 2K_c a + \ldots + nK_c^{n-1}a^{n-1}}{1 + K_c a + \ldots + K_c^{n-1}a^{n-1}} \qquad (8.12)$$

In Eqs. (8.10)-(8.12) for c_h, L, and $\bar{n}$, the quantity n determines the number of carbon atoms in the hydrocarbon in the synthesized

mixture whose molecular mass is the largest. It is better to determine the value of n from the results of an experiment because it depends on the type of catalyst used. An analysis of the expressions for c_h, L, $\bar{n}$, and also of the equilibrium constants given in Table 107 shows that the formation of low-molecular hydrocarbons is more favourable thermodynamically. That the Fischer-Tropsch synthesis can be employed for producing high-molecular hydrocarbons is explained by kinetic factors and does not contradict thermodynamic calculations. It is expedient to perform the latter only for the reactions observed in experiments, and not for all hypothetically possible ones.

Thermodynamic Analysis of Fischer-Tropsch Synthesis of Methane. Kinetic studies show that a number of reactions proceed in the synthesis of methane, namely,

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

$$2CO \rightarrow CO_2 + C \qquad (3)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (4) = (1) - (2)$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \qquad (5) = (1) + (2)$$

In thermodynamic analysis, account must be taken only of independent reactions (1)-(3) whose combination results in reactions (4) and (5).

The equilibrium compositions for a complex reaction including the simple steps (1)-(3) can be calculated by the methods described in Chap. 3. But for the specific case being considered, we can simplify the calculations by introducing the degrees of conversion of the CO by steps (1)-(3), i.e. y_1-y_3, respectively [66]. If we express the numbers of moles of the components and further the equilibrium constants $K_{x,1}$-$K_{x,3}$ in terms of y_1-y_3 and designate by δ_i the ratio of the number of moles of component i and CO in the initial mixture, we obtain the following system of equations for determining y_1-y_3:

$$\left.\begin{aligned}
K_{x,1} &= \frac{[\delta(CH_4)+y_1][\delta(H_2O)+y_1-y_2]\left[1+\delta(H_2)+\right.}{(1-y_1-y_2-y_3)[\delta(H_2)-3y_1+y_2]^3} \\
&\ldots\rightarrow \left.\frac{+\delta(CH_4)+\delta(H_2O)+\delta(CO)_2-2y_1-\frac{1}{2}y_2\right]^2}{} \\
K_{x,2} &= \frac{\left[\delta(CO_2)+y_2+\frac{1}{2}y_3\right][\delta(H_2)-3y_1+y_2]}{(1-y_1-y_2-y_3)[\delta(H_2O)+y_1-y_2]} \\
K_{x,3} &= \frac{\left[\delta(CO_2)+y_2+\frac{1}{2}y_3\right][1+\delta(H_2)+\delta(CH_4)+\delta(H_2O)}{(1-y_1-y_2-y_3)^2} \\
&\ldots\rightarrow \left.\frac{+\delta(CO_2)-2y_1-\frac{1}{2}y_2\right]}{}
\end{aligned}\right\} \qquad (8.13)$$

Table 108. **Equilibrium Degrees of Conversion y_i of CO by Independent Reactions in the Fischer-Tropsch Synthesis of Methane [at $\delta(H_2)$ equal to 1, 3, 5, and 10]**

T, K	y_i	p, MPa																			
		0.01				0.1				0.5				1.0				5.0			
		1	3	5	10	1	3	5	10	1	3	5	10	1	3	5	10	1	3	5	10
300	y_1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1
	y_1	0.499	0.999	≈1	≈1	0.499	0.999	≈1	≈1	0.499	0.999	≈1	≈1	0.499	0.999	≈1	≈1	0.499	0.999	≈1	≈1
	y_2	0.499	0.001	≈0	≈0	0.499	0.001	≈0	≈0	0.499	0.001	≈0	≈0	0.499	0.001	≈0	≈0	0.499	0.001	≈0	≈0
	y_1	0.332	≈1	≈1	≈1	0.332	≈1	≈1	≈1	0.332	≈1	≈1	≈1	0.332	≈1	≈1	≈1	0.332	≈1	≈1	≈1
	y_3	0.668	≈0	≈0	≈0	0.668	≈0	≈0	≈0	0.668	≈0	≈0	≈0	0.668	≈0	≈0	≈0	0.668	≈0	≈0	≈0
400	y_1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1
	y_1	0.498	0.995	≈1	≈1	0.498	0.998	≈1	≈1	0.498	0.999	≈1	≈1	0.498	0.999	≈1	≈1	0.498	≈1	≈1	≈1
	y_2	0.498	0.005	≈0	≈0	0.498	0.002	≈0	≈0	0.498	0.001	≈0	≈0	0.498	0.001	≈0	≈0	0.498	≈0	≈0	≈0
	y_1	0.332	0.996	≈1	≈1	0.332	0.998	≈1	≈1	0.332	0.999	≈1	≈1	0.332	≈1	≈1	≈1	0.332	≈1	≈1	≈1
	y_3	0.667	0.004	≈0	≈0	0.668	0.002	≈0	≈0	0.668	0.001	≈0	≈0	0.668	≈0	≈0	≈0	0.668	≈0	≈0	≈0
500	y_1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1
	y_1	0.498	0.962	≈1	≈1	0.499	0.985	≈1	≈1	0.499	0.992	≈1	≈1	0.499	0.994	≈1	≈1	0.499	0.997	≈1	≈1
	y_2	0.497	0.038	≈0	≈0	0.498	0.015	≈0	≈0	0.498	0.008	≈0	≈0	0.498	0.006	≈0	≈0	0.498	0.003	≈0	≈0
	y_1	0.325	0.966	≈1	≈1	0.331	0.987	≈1	≈1	0.332	0.994	≈1	≈1	0.332	0.995	≈1	≈1	0.333	0.998	≈1	≈1
	y_3	0.674	0.034	≈0	≈0	0.669	0.013	≈0	≈0	0.668	0.006	≈0	≈0	0.667	0.005	≈0	≈0	0.667	0.002	≈0	≈0

Table 108 (*concluded*)

T, K	y_i	p, MPa																			
		0.01				0.1				0.5				1.0				5.0			
		1	3	5	10	1	3	5	10	1	3	5	10	1	3	5	10	1	3	5	10
600	y_1	0.333	0.940	0.990	≈1	0.333	0.950	0.990	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1	0.333	≈1	≈1	≈1
	y_1	0.483	0.863	0.995	≈1	0.494	0.942	≈1	≈1	0.497	0.969	≈1	≈1	0.498	0.976	≈1	≈1	0.499	0.987	≈1	≈1
	y_2	0.473	0.134	0.005	≈0	0.488	0.058	≈0	≈0	0.493	0.031	≈0	≈0	0.494	0.024	≈0	≈0	0.496	0.013	≈0	≈0
	y_1	0.295	0.867	≈1	≈1	0.321	0.950	≈1	≈1	0.328	0.975	≈1	≈1	0.329	0.981	≈1	≈1	0.331	0.991	≈1	≈1
	y_3	0.682	0.121	≈0	≈0	0.672	0.048	≈0	≈0	0.669	0.024	≈0	≈0	0.669	0.018	≈0	≈0	0.668	0.009	≈0	≈0
700	y_1	0.285	0.690	0.905	0.980	0.310	0.875	0.995	≈1	0.333	0.965	≈1	≈1	0.333	0.990	≈1	≈1	0.330	≈1	≈1	≈1
	y_1	0.406	0.676	0.836	0.965	0.469	0.852	0.992	≈1	0.485	0.019	≈1	≈1	0.489	0.938	≈1	≈1	0.494	0.967	≈1	≈1
	y_2	0.377	0.249	0.119	0.019	0.477	0.136	0.006	≈0	0.469	0.078	≈0	≈0	0.476	0.060	≈0	≈0	0.486	0.033	≈0	≈0
	y_1	0.224	0.645	0.894	—	0.295	0.863	0.998	≈1	0.316	0.932	≈1	≈1	0.321	0.949	≈1	≈1	0.328	0.975	≈1	≈1
	y_3	0.523	0.166	0.021	—	0.622	0.095	≈0	≈0	0.647	0.055	≈0	≈0	0.653	0.042	≈0	≈0	0.660	0.023	≈0	≈0
800	y_1	0.125	0.300	0.430	0.600	0.305	0.850	0.990	0.995	0.330	0.955	0.995	≈1	0.333	0.965	0.997	≈1	0.333	0.985	≈1	≈1
	y_1	0.208	0.361	0.451	0.595	0.390	0.698	0.872	0.978	0.448	0.833	0.986	0.989	0.462	0.872	0.996	≈1	0.481	0.931	≈1	≈1
	y_2	0.173	0.178	0.144	0.086	0.341	0.201	0.075	0.008	0.407	0.138	0.010	≈0	0.426	0.112	0.003	≈0	0.457	0.064	≈0	≈0
	y_1	0.109	0.294	0.419	—	0.242	0.686	0.915	—	0.291	0.845	—	—	0.304	0.886	—	—	0.320	0.945	—	—
	y_3	0.104	0.039	0.018	—	0.342	0.069	0.060	—	0.493	0.059	—	—	0.538	0.052	—	—	0.606	0.034	—	—

The following equations can be used for the quantities $K_{x,1}$-$K_{x,3}$ in the region of temperatures of practical interest:

$$\left.\begin{aligned} \log K_{x,1} &= 2\log\left(\frac{p}{p^0}\right) - 12.3 + \frac{10\,800}{T} \\ \log K_{x,2} &= -1.69 + \frac{1867}{T} \\ \log K_{x,3} &= \log\left(\frac{p}{p^0}\right) - 11.2 + \frac{9100}{T} \end{aligned}\right\} \qquad (8.14)$$

A computer programme has been developed and calculations have been performed (see Sec. 3.5) to find y_1-y_3. Some of the results of these calculations are presented in Table 108.

If only reaction (1) proceeds (the lines of y_1 in Table 108), then with a stoichiometric ratio of CO and H_2 the thermodynamic restrictions manifest themselves only at 600-700 K, but at increased pressures and H_2:CO ratios the CO can be converted completely into methane even at 800 K. If reactions (1) and (2) proceed simultaneously (the lines of y_1 and y_2 in Table 108) and the H_2:CO ratio in the initial mixture is at least three, then about 4% of the CO will react by reaction (2) at 500 K and 25% (the highest value) at 700 K. In this case too, complete conversion of the CO into methane can be achieved, but more rigorous conditions are needed than when only reaction (1) is taken into consideration.

If reactions (1) and (3) proceed simultaneously (the lines of y_1 and y_3 in Table 108), then at 700 K about 17% of the CO can be converted by reaction (3) (the highest value). To suppress reaction (3), it is also necessary to employ increased pressures and dilution with hydrogen. But for temperatures above 700 K, the effect of the side reactions (2) and (3) cannot be disregarded.

Attention must be given to the features of the proceeding of a complex reaction under conditions of a lack of hydrogen [$\delta(H_2) = 1$]. In this case, the major part of the CO will participate in side reactions, and the fraction of the CO converted into methane will be lower than that converted into carbon and carbon dioxide.

It should be noted that in the Fischer-Tropsch synthesis of any hydrocarbon, it is necessary to consider a complex reaction including three simple ones, namely, the direct synthesis of a hydrocarbon, and reactions (2) and (3). A system similar to (8.13) must be solved, but the first equation should be written for the reaction

$$\nu_1 CO + \nu_2 H_2 \rightarrow C_{\nu_1}H_{2(\nu_2-\nu_1)} + \nu_1 H_2O$$

The terms determining the number of moles of the components and their sum change accordingly.

8.4. Synthesis of Hydrocarbons and Ethers from Methanol

Recent years have seen attention being given to the synthesis of hydrocarbons via methanol instead of directly from carbon monoxide and hydrogen. This makes it possible to use the well developed large-scale technology of methanol synthesis. The thermodynamics of producing methanol from carbon monoxide and hydrogen has been treated in Sec. 8.2.1. The production of hydrocarbons and ethers from methanol is quite simple technologically when a solid crystalline silica-alumina catalyst is employed having an increased silica: :alumina ratio. The merits of such two-step production of hydrocarbons consist in the possibility of controlling the methanol processing regime and in the production of hydrocarbons with a preset structure and molecular mass, namely, individual alkenes, aromatics, alkanes, and the components of petrol or diesel fuel. Let us consider the reactions resulting in the production of motor fuel components.

The oxygen content in methanol is about 53%, therefore its heat of combustion is not high, i.e., —21 370 kJ/kg, which is almost half that of petrol. To produce hydrocarbons with a high heat of combustion from methanol, reactions are used with the separation of all or part of the oxygen in water molecules. Table 109 presents the thermodynamic characteristics of representative reactions of producing alkenes when they are carried out in the ideal gas phase.

Table 109. **Reactions of Producing Alkenes in the Ideal Gas Phase**

Reaction	n	$-\Delta H^\circ$, kJ	$\log K^\circ_{p,\,300}$	$\log K^\circ_{p,\,800}$	Ratio of heats of combustion of product and feed stock
$5CH_3OH \rightarrow C_5H_{10}+5H_2O$	5	224	52	20	0.94
$6CH_3OH \rightarrow C_6H_{12}+6H_2O$	6	285	54	24	0.94
$10CH_3OH \rightarrow C_{10}H_{20}+10H_2O$	10	530	94	38	0.93
$16CH_3OH \rightarrow C_{16}H_{32}+16H_2O$	16	898	154	60	0.93

There are no thermodynamic restrictions to the synthesis of alkenes from methanol within quite a wide temperature interval, and the reaction proceeds with the evolution of heat. It is convenient to present the obtained data in the form of ΔH° and $\log K^\circ_p$ as a function of n, which gives a thermodynamic characteristic of the conversion of one CH_2 group to a hydrocarbon. For the production of normal 1-alkenes, we find:

$$\Delta H^\circ/n = -45-(n-5)\,\text{kJ},\quad \log K^\circ_{p,300}/n = 9.5,\quad \log K^\circ_{p,800}/n = 3.8$$

Thus, the evolution of heat per mole of carbon converted to a hydrocarbon is 45-55 kJ. The formed hydrocarbon evolves in combustion 6-7% less heat than the methanol used to produce it. Consequently, if there are no special reasons (for example, the need to produce a hydrocarbon for petrochemical syntheses), it is more efficient to produce energy by the direct combustion of methanol in an engine than by combustion of the hydrocarbon produced from it. To confirm what has been said above, Table 110 compares the characteristics of the production from methanol of hydrocarbons of various structure: alkenes, cycloalkanes, aromatics, and alkanes with six carbon atoms.

Table 110. **Comparison of the Characteristics of Producing Various Hydrocarbons from Methanol**

Reaction	$\Delta H^\circ/n$, kJ	$\log K^\circ_{p,300}$	$\log K^\circ_{p,800}$	Ratio of heats of combustion of products and feed stock
		n	n	
$6CH_3OH \rightarrow$ 1-hexene $+ 6H_2O$	48	9	3.3	0.94
$6CH_3OH \rightarrow$ cyclohexane $+ 6H_2O$	61	11	4.0	0.92
$6CH_3OH \rightarrow$ methylcyclopentane $+ 6H_2O$	58	11	4.2	0.92
$6CH_3OH \rightarrow$ benzene $+ 6H_2O + 3H_2$	27	8	5.2	0.77
$24CH_3OH \rightarrow$ 3 (isohexane) + benzene $+ 24H_2O$	58	11	4.4	0.92

It is possible thermodynamically to produce hydrocarbons of the indicated groups from methanol. Attention must be given to the high energy losses in the selective production of aromatics. This is why the synthesis of aromatics to use them as motor fuel components should be combined with the simultaneous use of the evolved hydrogen for the hydrogenation of alkenes. The last reaction in Table 110 is an example of such a complex process.

The simultaneous production of aromatics and cycloalkanes is not profitable from an energy standpoint because the evolved hydrogen is not utilized. Actually, the evolution of hydrogen signifies that in the scheme synthesis gas $\rightarrow$ methanol $\rightarrow$ hydrocarbons a part of the hydrogen is recirculated, which substantially increases the expenditure of energy.

The energy balance is improved if ethers are produced from the methanol instead of hydrocarbons by the reaction

$$n\,CH_3OH \rightarrow C_{n-1}H_{2(n-1)}OCH_3 + (n-1)\,H_2O$$

Calculations [66, 67] show that this reaction also proceeds thermodynamically like an irreversible one within a wide temperature interval, but the losses in the calorific value of the fuel will be about a half of those when hydrocarbons are produced—about 4%.

8.5. Syntheses of Acids and Aldehydes with the Use of CO

1. A number of authors have performed experimental and theoretical investigations of the production of organic compounds from carbon monoxide. The simplest of them are the reactions of synthesis of formaldehyde and formic acid:

$$CO + H_2 \rightarrow H_2CO$$
$$CO + H_2O \rightarrow HCOOH$$

Thermodynamic analysis has shown [4] that the synthesis of formaldehyde even at the low temperatures and high pressures favouring this reaction can involve only fractions of a per cent of the CO. Equilibrium for the production of formic acid is more favourable. If the reaction is conducted in the gas phase, the conversion of the CO will be negligible, but in a gas-liquid system (H_2O and HCOOH are liquid), the degrees of conversion become noticeable, and the synthesis of formic acid was successfully conducted at 300-500 K and pressures up to 10 MPa in the presence of catalysts. Here (and also in the reactions involving CO_2—see Sec. 8.6), a high thermodynamic efficiency of the gas-liquid reactions is observed in comparison with gas-phase ones.

For the gas-phase reaction of producing formic acid at 300 K, $\log K_p^\circ = -2.23$, while for the gas-liquid reaction, K_p° is 1.5 orders of magnitude higher. Since

$$K_p^\circ = \frac{x\,(\mathrm{HCOOH})}{x\,(\mathrm{H_2O})}\,\frac{p^\circ}{p\,(\mathrm{CO})}\,, \text{ then } \frac{x\,(\mathrm{HCOOH})}{x\,(\mathrm{H_2O})} = K_p^\circ\,\frac{p\,(\mathrm{CO})}{p^\circ}$$

At $p(\mathrm{CO}) = 50$ to $100p^\circ$ and moderate temperatures, the ratio of the mole fractions in the solution $x(\mathrm{HCOOH})/x(\mathrm{H_2O})$ can be several units.

2. The reaction of producing benzaldehyde from benzene and CO is of practical importance. If this reaction is conducted in the gas phase, the conversion of the benzene will be negligibly small. But, as above, for the gas-liquid reaction (C_6H_6 and C_6H_5CHO are liquids) equilibrium is more favourable, namely, the values of K_p° are as follows [26]:

T, K	300	325	375
K_p°	30×10^{-3}	12.5×10^{-3}	2.7×10^{-3}

For this reaction, we have

$$K_p^\circ = \frac{x\,(\mathrm{C_6H_5CHO})}{x\,(\mathrm{C_6H_6})}\,\frac{p^\circ}{p\,(\mathrm{CO})}\,, \quad \frac{x\,(\mathrm{C_6H_5CHO})}{x\,(\mathrm{C_6H_6})} = K_p^\circ\,\frac{p\,(\mathrm{CO})}{p^\circ}$$

Stull [26] estimates the possible degree of conversion of benzene at 325 K to be about 2%, but he evidently has in view the reaction at

atmospheric pressure. If it is conducted at high CO pressures, however, the degree of conversion will be much higher:

T, K		300			325			375	
p(CO), MPa	1.0	1	10	0.1	1	10	0.1	1	10
Equilibrium degree of conversion of benzene to benzaldehyde, %	3	23	75	1	11	55	0.3	3	23

3. The reactions of ethylene and acetylene with CO and H_2O make it possible to produce organic acids. They are carried out at temperatures of 300-800 K in the presence of catalysts in either a gas-phase or gas-liquid system.

For the reaction $C_2H_4 + CO + H_2O \rightarrow CH_3CH_2COOH$, when the temperature is raised from 300 to 600 K, the value of K_p° drops from about 10^{15} (at 300 K) to about 10^2 (at 500 K) and 10^{-2} (at 600 K). Hence, the carrying out of this reaction at elevated temperatures requires the use of high CO pressures (it is conducted at 10-100 MPa and at temperatures up to 800 K).

The reaction $C_2H_2 + CO + H_2O \rightarrow CH_2{=}CHCOOH$ is possible thermodynamically as an irreversible one within the temperature interval 300-500 K ($K_{p,300}^\circ = 10^{22}$, $K_{p,500}^\circ = 10^{7.6}$), which is of practical interest, and requires no high CO pressures—it is conducted at 300-400 K and 0.1-1 MPa. In these two cases, an empirical search resulted in the finding of thermodynamically favourable conditions.

4. The reaction of CO with methanol yields acetic acid. The reaction $CH_3OH + CO \rightarrow CH_3OOH$ is conducted in the gas phase at 10-70 MPa in the presence of catalysts. The equilibrium constant K_p° of this reaction decreases with increasing temperature and for 300, 500, and 600 K is 10^{13}, $10^{4.8}$, and $10^{2.6}$, respectively. Consequently, the conducting of this reaction at increased CO pressures is explained not by thermodynamic, but by kinetic considerations, namely, the need to activate the catalyst.

8.6. Syntheses Based on CO_2

Syntheses Based on CO_2, Carbonates, Hydrogen, Coal, and Steam. The supplies of carbonates in the Earth's crust are higher by several orders of magnitude than those of organic fuel, and are renewed; carbon dioxide is a residue of modern production processes and is utilized only to a small extent. Let us therefore consider the thermodynamic probability and energy efficiency of the syntheses of organic compounds on the basis of CO_2 or carbonates with the involvement in the synthesis of hydrogen, steam, and coal. Attention was given to the expediency of such syntheses in the investigations of Ya. Paukin because, owing to the availability of the raw material, they can be achieved in large-scale production processes. For this purpose, the heats ΔH° and equilibrium constants of the reactions of

producing an acid (HCOOH), alcohol (CH_3OH), and a hydrocarbon (CH_4) from CO_2 have been determined for low (300 K) and high (1000 K) temperatures for the following variants:

I—reactions of CO_2 with hydrogen with the evolution of only H_2O;

II—reactions of CO_2 with hydrogen with the evolution of H_2O and CO;

III—reactions of CO_2 with coal and hydrogen without the evolution of CO;

IV—reactions of CO_2 with coal and hydrogen with the evolution of CO;

V—reactions of CO_2 with coal and water;

VI—reactions of $CaCO_3$ with hydrogen and water.

Some results are presented in Table 111.

It pays to carry out reactions if $\log K_p \geqslant -1$. Examination of the data in Table 111 reveals that the reactions of CO_2 with hydrogen leading to the formation of hydrocarbons (Nos. 3, 6, 8, and 10) are possible thermodynamically, and they will be facilitated by low temperatures (the reactions are exothermic). An exception is the endothermic reaction of CO_2 with coal and water (No. 15), which can be carried out at high temperatures.

It is good practice to attempt to conduct reactions of hydrocarbon synthesis from CO_2 with the simultaneous conversion of part of the CO_2 into CO, but here the use of hydrogen for producing one mole of a hydrocarbon does not lower noticeably. The synthesis of hydrocarbons is also possible in the presence of coal; here 1.5-2 times less hydrogen is needed than in the absence of coal.

It should be noted that at high temperatures (1000 K) hydrocarbons can also be produced from CO_2 without hydrogen, by a reaction with coal and steam (reaction 15). Although this reaction is highly endothermic, it may be efficient on an industrial scale as a result of using the heat of flue gases.

The reactions of producing alcohols from CO_2 involve greater thermodynamic difficulties than the production of hydrocarbons. Among the reactions listed in Table 111, reaction 2 can be recommended for this purpose, but the thermodynamic restrictions even at low temperatures will be substantial, while the use of hydrogen will be higher by 30% than when CO is used. As regards the production of acids, it requires the use of a wider range of reactants than those considered above. This can be confirmed by the fact that, as shown by experimental investigations, only negligible amounts of formic acid could be obtained from a mixture of CO_2 and H_2.

The use of calcium carbonate as a source of carbon dioxide makes it possible to carry out the same reactions as with the CO_2 reactant, but they require higher temperatures. These reactions are naturally more endothermic.

Table 111. **Heats and Equilibrium Constants for Reactions of Organic Compound Production from CO_2 and $CaCO_3$**

Reaction		300 K		1000 K		Moles of H_2 used per mole of CH_4
		$\Delta H°$, kJ	log $K_p°$	$\Delta H°$, kJ	log $K_p°$	
$CO_2+H_2 \xrightarrow{1} HCOOH$	I	−14.73	−7.6	8.58	−6.1	—
$*CO_2+3H_2 \xrightarrow{2} CH_3OH+H_2O$	I	−49.6	+0.07	−70.5	−7.7	—
$*CO_2+4H_2 \xrightarrow{3} CH_4+2H_2O$	I	−165.1	+19.2	−190.6	+0.4	4
$2CO_2+2H_2 \xrightarrow{4} HCOOH+CO+H_2O$	II	39.3	−12.6	42.9	−6.3	—
$2CO_2+4H_2 \xrightarrow{5} CH_3OH+CO+2H_2O$	II	−8.4	−5.6	−35.8	−7.8	—
$2CO_2+5H_2 \xrightarrow{6} CH_4+CO+3H_2O$	II	−123.8	+14.2	−66.8	+0.3	5
$CO_2+C+4H_2 \xrightarrow{7} 2CH_3OH$	III	−9.0	−12	−40.0	−14.8	—
$*CO_2+C+6H_2 \xrightarrow{8} 2CH_4+2H_2O$	III	−240	27.4	−280	1.4	3
$CO_2+C+2H_2 \xrightarrow{9} CH_3OH+CO$	IV	81.6	−16.5	65.3	−7.1	—
$*CO_2+C+3H_2 \xrightarrow{10} CH_4+CO+H_2O$	IV	−33.8	+3.3	−54.8	+0.9	3
$CO_2+H_2O \xrightarrow{11} HCOOH+\frac{1}{2}O_2$	V	256	—	256	—	—
$CO_2+2H_2O \xrightarrow{12} CH_3OH+\frac{3}{2}O_2$	V	676	—	700	—	—
$CO_2+C+H_2O \xrightarrow{13} HCOOH+CO$	V	146	−23	144	−5.6	—
$CO_2+3C+2H_2O \xrightarrow{14} CH_3OH+3CO$	V	187	−35	175	−13	—
$*CO_2+4C+2H_2O \xrightarrow{15} CH_4+4CO$	V	360	−44	353	+2.1	0

Table 111 (*concluded*)

Reaction		300 K		1000 K		Moles of H_2 used per mole of CH_4
		ΔH°, kJ	$\log K_p^\circ$	ΔH°, kJ	$\log K_p^\circ$	
$*CaCO_3 + 4H_2 \xrightarrow{16} CH_4 + 2H_2O + CaO$	VI	13	—2.8	—12	—0.5	4
$*2CaCO_3 + 5H_2 \xrightarrow{17} CH_4 + CO + 3H_2O + 2CaO$	VI	232	—7.1	290	—0.6	5
$*CaCO_3 + C + 6H_2 \xrightarrow{18} 2CH_4 + 2H_2O + CaO$	VI	—62	5.4	—102	+0.5	3
$*CaCO_3 + 4C + 2H_2O \xrightarrow{19} CH_4 + 4CO + CaO$	VI	538	—	530	+1.3	0

* These reactions can proceed with appreciable degrees of conversion at 300 or 1000 K.

In all cases, the yields of the target products grow when the pressure is increased.

Syntheses Based on Reactions of CO_2 with Hydrocarbons. A number of reactions of CO_2 with hydrocarbons are of interest for organic synthesis. For example, the reaction $C_2H_4 + CO_2 \rightarrow CH_2{=}CHCOOH$ is employed for producing acrylic acid. Let us consider the thermodynamic characteristics of some reactions of CO_2 with hydrocarbons.

For the gas-phase reaction of CO_2 with ethylene, $\log K^\circ_{p,300} = -7$ and $\log K^\circ_{p,800} = -6.5$, i.e. the temperature has only a slight effect. The effect of the pressure is greater: at 0.1 MPa for the gas-phase reaction, $K_{x,300} = 10^{-7}$, while at 10 MPa, $K_{x,300} \approx 10^{-5}$. At the same time, the thermodynamics improves appreciably if the reaction is conducted in a gas-liquid system. For this system, K_p° is of the order of magnitude of 10^{-2}, and substantial degrees of conversion of ethylene to acrylic acid are possible. Similarly for the reaction $C_6H_6 + CO_2 \rightarrow C_6H_5COOH$ when conducted in the gas phase, $\log K^\circ_{p,300} = -9$, while if a solid or liquid acid forms, $\log K^\circ_{p,300} = -2.9$. The conducting of such a reaction at an increased pressure (10 MPa) is possible thermodynamically with considerable degrees of conversion.

The reaction of CO_2 with acetylene with the formation of an alkyne acid is the most favourable from thermodynamic considerations. This reaction is probable thermodynamically (degrees of conversion above 70%) in both the liquid and gas phase.

Thus, for the reaction of CO_2 with unsaturated hydrocarbons or aromatics, gas-liquid systems and increased pressures should be used. The effect of the temperature on these reactions is not great.

The reaction of carbon dioxide with methane is of considerable practical interest. The possible reactions and their constants are presented in Table 112.

Table 112. **Equilibrium Constants of CO_2 Reactions with Methane**

Reaction	log K_p° at T, K		
	400	800	1000
$CH_4 + CO_2 \rightarrow CH_3OH + CO$	−25.3	−8.3	−6.2
$CH_4 + CO_2 \rightarrow CH_3COOH$	−10.5	−8.3	−7.9
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	−18.8	−2.1	1.3
$CH_4 + CO_2 \rightarrow H_2C{=}CO + H_2O$	−20.0	−9.0	−6.8

A thermodynamically possible reaction of producing CO and H_2 is treated in Sec. 8.3. At high temperatures, the reaction of methanol production is of interest. For this reaction at 1300 K, we have $\log K_p^\circ = -4$. This signifies that at a pressure of 10 MPa and a molar ratio $CO_2{:}CH_4 = 1$, the degree of conversion of methane is about 10%, while at $CO_2 : CH_4 = 2$, it is about 15%. The reaction is endothermic and requires about 157 kJ per mole of methane.

Chapter 9

Thermodynamics of Chemical Processes in Natural Gas Treatment

The main components of natural gas are methane, hydrogen sulphide, and carbon dioxide. Information on some reactions of carbon dioxide, the production of hydrogen and synthesis gas from methane, and on the reaction of methane with saturated (disproportionation) and unsaturated (cracking) hydrocarbons is given on preceding pages. Below we consider the thermodynamic characteristics of hydrogen sulphide utilization—the Klaus process—and of syntheses based on methane.

9.1. Reactions of Producing Elemental Sulphur from Hydrogen Sulphide

The hydrocarbon gases of gas and gas-condensate fields and the accompanying gases of petroleum refining and coal gasification contain appreciable [sometimes up to 30% (mol)] amounts of hydrogen sulphide.

After the separation of the hydrogen sulphide, it is converted into sulphur by what is known as the Klaus reaction:

$$H_2S + 0.5O_2 \rightarrow H_2O + S \qquad \text{(XXVI)}$$

The technology of producing elementary sulphur includes a number of steps.

At 1200-1600 K, the hydrogen sulphide is burned (a high-temperature zone—the reaction furnace) with the formation of sulphur, SO_2, water, and a number of other compounds. At 800-1100 K, the mixture of gases is cooled with the further formation of sulphur, SO_2, and water (a moderate temperature zone—the waste-heat boiler and the technological lines up to the first sulphur condenser). At 500-700 K, the hydrogen sulphide and SO_2 are reacted on a catalyst (a low-temperature zone—the catalytic reactors).

In analysing the possible results of the Klaus process, thermodynamic calculations of the equilibrium constants and equilibrium compositions are used because at the process temperatures the experimental yields of the products are close to the equilibrium ones.

The analysis of the process requires the establishment of the composition of the sulphur modifications formed in the various apparatuses of the equipment and the determination of the thermodynamically most stable modification. There are seven sulphur modifications from S_2 to S_8. The most stable of them are S_2, S_6, and S_8.

We have performed thermodynamic calculations of the equilibrium of various sulphur modifications. We used thermodynamic data that seemed to be the most reliable [66].

Table 113 presents the equilibrium constants for the mutual transitions of various sulphur modifications at different temperatures.

Table 113. **Equilibrium Constants K_p° at Various Temperatures for Mutual Transitions of Various Sulphur Modifications**

Temperature, K	Equilibrium constants K_p° of transition			
	$2S \rightarrow S_2$	$2S_2 \rightarrow S_4$	$S_2+S_4 \rightarrow S_6$	$2S_4 \rightarrow S_8$
500	$> 10^{15}$	1.652×10^{4}	2.742×10^{9}	4.150×10^{9}
700	$> 10^{15}$	4.227×10^{0}	4.699×10^{3}	4.930×10^{4}
900	$> 10^{15}$	4.477×10^{-2}	1.175×10^{1}	1.047×10^{2}
1100	1.849×10^{14}	2.570×10^{-3}	2.767×10^{-1}	2.275×10^{0}
1200	3.597×10^{12}	8.851×10^{-4}	6.887×10^{-2}	5.559×10^{-1}
1400	1.278×10^{9}	1.683×10^{-4}	7.962×10^{-3}	6.295×10^{-2}
1600	6.902×10^{7}	4.875×10^{-5}	1.614×10^{-3}	1.276×10^{-2}

Examination of Table 113 reveals that in the high-temperature zone the presence of sulphur in the form of the modification S_2 is the most probable thermodynamically. The atomic sulphur that may form as a result of the high-temperature dissociation of H_2S

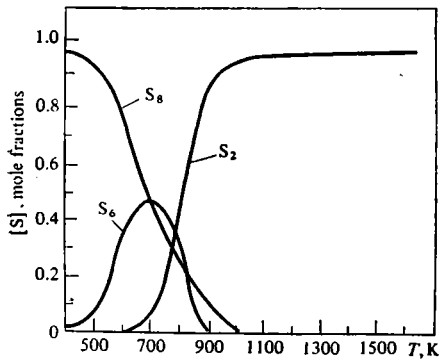


Fig. 40. Concentration of sulphur modifications S_2, S_6, and S_8 in an equilibrium mixture at various temperatures

[68] associates into S_2 molecules. The modification S_4 appears only in very small amounts.

In the moderate-temperature zone, the sulphur modifications S_2-S_8 can exist. At relatively low temperatures, S_8 will be the main modification.

Thus, it is necessary to determine the amounts of the different sulphur modifications only for the moderate-temperature zone. The fractions of the main modifications in an equilibrium mixture are depicted in Fig. 40.

The theoretical data for the low-temperature zone are consistent with experimental data [68], which show that in the zone of low temperatures the sulphur vapour consists mainly of S_8 molecules. Consequently, the reaction of producing sulphur from hydrogen sulphide is a complex one and should be written in the form

$$H_2S + 0.5O_2 \rightarrow \frac{1}{n} S_n + H_2O \qquad (1)$$

where n varies from two to eight.

The thermodynamic calculations for this complex reaction have been performed by a number of authors and are given, for example, in [64]. Table 114 contains data on the equilibrium degree of conversion of H_2S.

The data in Table 114 have been obtained for a molar ratio of $H_2S:O_2$ in the initial mixture equal to two. The appearance of a minimum near 800 K is associated with a change in the predominating sulphur modification. It is not difficult to note that the influence of the pressure is low.

It was found that in catalytic processes (at moderate temperatures) the results of calculations and experiments are close, while in thermal processes (at high temperatures) the experimental degrees of conversion can be substantially higher than the calculated ones. This is explained by two reasons: (a) all the sulphur modifications do not always form, and (b) secondary reactions acquire significance. The second reason is more important. Thus, the Klaus reaction proceeds either in one or in two steps, namely, part of the H_2S in the presence of oxygen is oxidized to SO_2:

$$H_2S + 1.5O_2 \rightarrow H_2O + SO_2 \qquad (2)$$

Table 114. **Equilibrium Degree of Conversion of Hydrogen Sulphide to Various Sulphur Modifications**

Temperature, K	Equilibrium degree of conversion of H_2S to various sulphur modifications (in %) at pressures, MPa			
	0.05	0.1	0.2	0.1 (after removal of 70% of the sulphur)
400	≈ 100	≈ 100	≈ 100	≈ 100
600	82	85	87	89
800	54	55	58	—
1000	62	58	55	—
1200	70	66	64	—
1400	74	72	70	
1600	76	75	72	

The formed SO_2 also reacts with H_2S with the production of sulphur:

$$2H_2S + SO_2 \rightarrow 2H_2O + \frac{3}{n} S_n \quad (3)$$

Other reactions also proceed. Acid gases contain hydrocarbons whose oxidation yields CO and CO_2. The following are the most important reactions of hydrocarbons (methane), CO, and CO_2 in the Klaus process:

$$CH_4 + \frac{2}{n} S_n \rightarrow CS_2 + 2H_2 \quad (4)$$

$$CH_4 + SO_2 \rightarrow COS + H_2O + H_2 \quad (5)$$

$$CO_2 + H_2S \rightarrow COS + H_2O \quad (6)$$

$$CO_2 + \frac{3}{n} S_n \rightarrow CS_2 + SO_2 \quad (7)$$

$$2CO_2 + \frac{1}{n} S_n \rightarrow 2CO + SO_2 \quad (8)$$

$$CO_2 + SO_2 \rightarrow COS + 1.5O_2 \quad (9)$$

$$CO + \frac{1}{n} S_n \rightarrow COS \quad (10)$$

$$2CO + \frac{2}{n} S_n \rightarrow CO_2 + CS_2 \quad (11)$$

$$CO + 2H_2S \rightarrow CS_2 + H_2O + H_2 \quad (12)$$

Although not all of these reactions are independent [summing of reactions (2) and (3) yields reaction (1), and so on], and when calculating equilibrium their number can be reduced, it is clear that the conversion of H_2S in the Klaus process depends not only on the temperature, pressure, and the H_2S:O_2 ratio, but also on the content and molecular mass of the hydrocarbon gases, CO_2, H_2O, etc.

Recent years have seen the calculations of complex equilibrium of the Klaus process by minimization of the Gibbs energy of the system (see Chap. 3). The calculations were performed for a real raw material and for a process occurring consecutively in a furnace, a waste-heat boiler, and three consecutive "catalytic reactor-condenser" sections. Table 115 presents the results of equilibrium calculations.

Table 115. **Variants of Calculations of Sulphur Extraction from an Acid Gas [Composition of the Raw Material (mol %): H_2S 89.72, CO_2 4.98, CH_4 0.8, H_2O 4.5]**

Item	Variants *			
	A	B	C	D
Furnace and waste-heat boiler:				
extraction, %	99.39	71.52	59.64	60.44
Reactor No. 1:				
T_{in}, K	—	502	516	516
T_{out}, K	—	635	600	600
extraction, %	—	13.92	28.47	29.03
Reactor No. 2:				
T_{in}, K	—	489	482	—
T_{out}, K	—	522	510	—
extraction, %	—	10.29	8.00	—
Reactor No. 3:				
T_{in}, K	—	456	447	—
T_{out}, K	—	465	456	—
extraction, %	—	2.58	2.04	—
Total sulphur extraction, %	99.39	98.31	98.15	89.47

* A — thermodynamic equilibrium, all modifications are taken into account; B — reactions of CO, COS, H_2, H_2O, H_2S, and SO_2 do not proceed in the condensers; C — reactions of H_2S and SO_2 do not proceed in the condensers; D — reactions of H_2S and SO_2 are absent (as in variant C); mass and heat changes are absent in the condenser.

Variant B is the closest to the conditions in a real process. The calculations show that the fraction of unextracted sulphur is quite noticeable (1.69%).

Of interest are the data on the need to take account of the sulphur modifications in the calculations. If the formation of all the sulphur modifications is taken into account, the degree of extraction is 96.94%, while if only S_2, S_6, and S_8 are considered, it is 96.75%; these figures are virtually indistinguishable. The same is illustrated by data on the equilibrium composition of the end (tail) gases in the process (Table 116).

Table 116. **Composition of End Gases (mole fractions)**

Components	Industrial acid gas		Pure hydrogen sulphide	
	all S modifications	S_2, S_6, S_8	all S modifications	S_2, S_6, S_8
Carbon monoxide	0.020 335	0.020 333	—	—
Carbon oxysulphide	0.001 148	0.001 149	—	—
Carbon dioxide	0.074 305	0.074 296	—	—
Carbon disulphide	0.000 005	0.000 005	—	—
Hydrogen	0.031 512	0.031 508	0.046 84	0.046 81
Water	0.309 422	0.309 169	0.328 47	0.328 09
Hydrogen sulphide	0.001 673	0.001 906	0.001 97	0.002 29
Nitrogen	0.560 541	0.560 478	0.621 51	0.621 45
Sulphur dioxide	0.000 844	0.000 961	0.000 99	0.001 16
Sulphur:				
S_5	0.000 001	—	—	—
S_6	0.000 036	0.000 036	0.000 04	0.000 04
S_7	0.000 020	—	0.000 02	—
S_8	0.000 158	0.000 159	0.000 16	0.000 16

Thermodynamic analysis made it possible to determine the effect of the composition of acid gas on the degree of conversion of H_2S. Table 117 gives the compositions of the gas at the outlet from the furnace for an industrial acid gas (the basic variant) and a gas containing increased amounts of one of the impurities. The least "harmful" impurity is methane, but any impurity lowers the degree of conversion of hydrogen sulphide to sulphur. Calculations also showed that the equilibrium content of COS and CS_2 is considerably lower than that observed in experiments [0.5-2% (mol) relative to the dry gas after removal of the sulphur]. This makes kinetic improvement of the process expedient.

9.2. Thermodynamic Probability of Chemical Methane-Based Syntheses

The use of methane for chemical syntheses at present is based on the intermediate production of synthesis gas. Here we shall deal with other reactions of methane for which scientific research is in hand.

Thermocatalytic Processes. Methane is thermodynamically more stable than other hydrocarbons. Only acetylene is more stable than it at high temperatures. For purposes of illustration, Table 118 presents data on log K_p° for the gas-phase reactions of producing hydrocarbons from methane.

The data for 1500 K in Table 118 can be considered only as approximate because the errors in determining log $K_{p,f}^\circ$ used to evaluate

Table 117. **Influence of Impurities in an Acid Gas on the Klaus Process**

Item	Variants of acid gas composition *					
	basic	A	B	C	D	E
Composition of acid gas, % (mol):						
hydrogen sulphide	89.72	49.84	20.00	85.74	76.27	70.45
carbon dioxide	4.98	45.21	75.32	4.76	4.23	3.91
methane	0.80	0.44	0.18	5.00	15.00	0.63
water	4.50	4.50	4.50	4.50	4.50	25.00
Temperature in furnace, K	1524	1253	883	1592	1712	1444
Composition of gas at furnace outlet, % (mol):						
carbon monoxide	0.46	1.22	0.052	0.88	1.87	0.29
carbon oxysulphide	0.19	0.19	0.21	0.025	0.028	0.016
carbon dioxide	1.29	18.88	50.05	1.82	2.57	1.3292
carbon disulphide	6.7×10^{-5}	4.8×10^{-4}	2.0×10^{-4}	8.0×10^{-5}	6.0×10^{-5}	4.8×10^{-5}
ammonia	3.5×10^{-5}	1.1×10^{-5}	6.5×10^{-5}	3.6×10^{-5}	3.6×10^{-5}	3.4×10^{-5}
nitrogen oxide	4.3×10^{-6}	3.7×10^{-8}	5.0×10^{-13}	1.1×10^{-5}	5.5×10^{-5}	1.3×10^{-6}
nitrogen dioxide	8.4×10^{-13}	1×10^{-13}	10^{-13}	3.5×10^{-12}	3.7×10^{-11}	1.5×10^{-13}
nitrous sulphur	1.6×10^{-5}	4.1×10^{-7}	6.6×10^{-11}	3.0×10^{-5}	7.5×10^{-5}	6.0×10^{-6}
hydrogen cyanide	2.2×10^{-8}	8.5×10^{-9}	4.1×10^{-12}	5.4×10^{-8}	1.6×10^{-7}	8.7×10^{-9}
Conversion in furnace, %	71.52	64.97	49.17	68.51	65.75	64.1

* Variants A and B are distinguished by an increased content of CO_2, C and D – of CH_4, and E – of H_2O.

log K_p° for the listed reactions are appreciable. At temperatures up to 1000 K and standard pressure, a degree of conversion of methane to ethylene of about 1% corresponds to the cited values of the equilibrium constants. The degrees of conversion to other hydrocarbons are still lower.

Table 118. **Values of log K_p° for Various Temperatures for Gas-Phase Reactions of Producing Hydrocarbons from Methane**

Reaction	log K_p° at T, K			
	300	700	1000	1500
$2CH_4 \rightarrow C_2H_6 + H_2$	—12	—9	—3.7	—2.4
$2CH_4 \rightarrow C_2H_4 + 2H_2$	—29	—9	—4.2	—0.3
$2CH_4 \rightarrow C_2H_2 + 3H_2$	—54	—16	—6.2	0.2
$3CH_4 \rightarrow C_3H_4 + 4H_2$ (propadiene)	—62	—19	—9.4	—1.4
$6CH_4 \rightarrow C_6H_6 + 9H_2$ (benzene)	—76	—21	—7.6	—

In the presence of zeolite-containing catalysts, ethylene and benzene are obtained with a yield exceeding 1%. This is due to the fact that if the conversion of methane proceeds with the simultaneous evolution of hydrogen and carbon, the thermodynamic probability of the reactions grows. Thus, when ethylene is produced by the reaction $3CH_4 \rightarrow C_2H_4 + 4H_2 + C$, we find $\log K_{p,1000}^\circ = -3.2$, while for the reaction $4CH_4 \rightarrow C_2H_4 + 6H_2 + 2C$, we find $\log K_{p,1000}^\circ = -2.2$. In the latter case, the degree of conversion of methane to ethylene reaches 2%. The same also relates to reactions with the production of benzene.

Thermodynamic analysis enables us to conclude that the production of aromatics or alkenes from methane at moderate temperatures will be attended by a high degree of coke formation and, possibly, by low degrees of conversion.

The production of acetylene from methane, on the other hand, is thermodynamically efficient at high temperatures. At 1500 K and standard pressure, the equilibrium degree of conversion of methane to acetylene is about 70%. Hence, the two-step synthesis of alkenes and aromatics from methane is possible thermodynamically, namely, at high temperatures acetylene is produced from the methane, and at relatively low ones the acetylene is converted to alkenes or aromatics.

Reactions of Methane with Oxygen-Containing Inorganic Compounds. Any reaction of methane with oxygen [with the formation of CH_3OH, CH_2O, $(CH_3)_2O$, CO, CO_2, etc.] is thermodynamically probable with practically complete using up of the reactants. Since

hydrocarbons of various groups can be produced from methanol (see Sec. 8.4), both two-step (scheme A) and one-step (scheme B) syntheses are possible thermodynamically:

$$CH_4 \xrightarrow{+O_2} CH_3OH \begin{cases} \rightarrow \text{hydrocarbons} \\ \rightarrow \text{oxygen-containing compounds} \end{cases} \qquad \text{(scheme A)}$$

$$CH_4 \xrightarrow{+O_2} \begin{cases} \rightarrow \text{hydrocarbons} \\ \rightarrow \text{oxygen-containing compounds} \end{cases} \qquad \text{(scheme B)}$$

In both schemes, the reactions are attended by the evolution of water; part of the methane will be oxidized to CO and CO_2.

The direct synthesis of methanol from methane without the use of oxygen, for example, by the reaction $CH_4 + CO_2 \rightarrow CH_3OH + CO$, is undoubtedly of scientific and practical interest. The indicated endothermic reaction (its enthalpy is about 160 kJ) should be more selective from a kinetic standpoint than the reaction of methane with oxygen. But this endothermic reaction (like other reactions of methane and carbon dioxide such as $CH_4 + CO_2 \rightarrow CH_3COOH$) is not efficient thermodynamically up to 1000 K ($\log K^{\circ}_{p,1000} = -6.3$). The thermodynamic probability of another "alluring" reaction, i.e. $CH_4 + H_2O \rightarrow CH_3OH + H_2$, is just as low.

Only at 1500 K does the equilibrium constant of the reaction $CH_4 + CO_2 \rightarrow CH_3OH + CO$ become appreciable; $\log K^{\circ}_{p,1500} \approx \approx -2.4$. This signifies that at standard pressure the degree of conversion of methane can be 3.4% if the molar ratio CO_2:CH_4 in the initial mixture is unity. An increase in the molar ratio up to 10 (or its decrease to 0.1) enables one to increase the yield of methanol relative to the CH_4 (or CO_2) to about 18%. Such synthesis can be the object of scientific research, but one must have in view the approximate nature of the calculations for a temperature of 1500 K.

Other inorganic oxygen-containing compounds can be "mild" oxidizing agents of methane. Below are given reactions which in the temperature interval 300-1000 K can proceed virtually to the end:

$$CH_4 + SO_2 \rightarrow HCOOH + H_2S$$
$$CH_4 + SO_3 \rightarrow CH_3OH + SO_2$$
$$CH_4 + SO_3 \rightarrow HCOOH + H_2O + S$$
$$CH_4 + NO \rightarrow CH_3OH + 0.5N_2$$
$$CH_4 + NO_2 \rightarrow CH_3OH + NO$$

The reactions of producing oxygen or nitrogen derivatives when methane is reacted with nitric acid proceed virtually to the end:

$$CH_4 + 2HNO_3 \rightarrow CH_3OH + H_2O + 2NO_2$$
$$CH_4 + HNO_3 \rightarrow CH_3NO_2 + H_2O$$

Reactions with Halogens, Sulphur, and Their Compounds. Reactions of methane with halogens (Hal) of the type

$$CH_4 + Hal_2 \rightarrow CH_3Hal + HHal$$
$$CH_4 + 2Hal_2 \rightarrow CH_2Hal_2 + 2HHal$$
$$CH_4 + 3Hal_2 \rightarrow CHHal_3 + 3HHal$$
$$CH_4 + 4Hal_2 \rightarrow CHal_4 + 4HHal$$

proceed virtually to the end at 300-1000 K. Reactions with various sulphur modifications (see Sec. 9.1) with the formation of thiols or carbon disulphide are also practically irreversible:

$$CH_4 + S \rightarrow CH_3SH$$
$$CH_4 + 4S \rightarrow CS_2 + 2H_2S$$

As regards reactions with hydrogen halides or hydrogen sulphide, if these reactions are attended by the evolution of hydrogen ($CH_4 + H_2S \rightarrow CH_3SH + H_2$), they are reversible relative to hydrogenolysis and have been treated in Chapter 7.

There are no thermodynamic hindrances for reactions of alkylation of methane with alkyl or aryl halides, such as

$$CH_4 + RHal \rightarrow CH_3R + HHal$$
$$CH_4 + ArHal \rightarrow CH_3Ar + HHal$$

or with very simple inorganic halogen derivatives, such as

$$CH_4 + COCl_2 \rightarrow CH_3Cl + CO + HCl$$
$$CH_4 + SO_2Cl_2 \rightarrow CH_3Cl + SO_2 + HCl$$

In general, reactions of methane with any halogen derivatives do not usually involve thermodynamic hindrances if they are attended by the evolution of HHal.

Appendix 1

Methods of Calculating the Standard Thermodynamic Functions of Hydrocarbons and Their Derivatives

A number of reference books, for example [4, 26], contain tables of the standard thermodynamic functions of hydrocarbons and their derivatives. It is impossible to provide such tables for all possible compounds because their number is too large. For example, there are 309 alkanes with from one to 11 carbon atoms, 48 alkenes with the formula C_7H_{14}, and so on. This is why greater and greater significance is being acquired by universal methods of calculating ΔH_f°, S°, C_p°, ΔG_f°, and $\log K_{p,f}^\circ$ for hydrocarbons and their derivatives. These methods are based on the constancy of the changes in the functions when going over from one structure of an organic compound to another, and they are chiefly semi-empirical ones. This does not detract from their effectiveness, however. They are mainly intended for calculating the properties of substances in the state of an ideal gas. Below we consider the most widespread methods, namely, the substitution of CH_3 groups for hydrogen and of functional groups for CH_3 ones (the method of Andersen, Bayer, and Watson), and the method of group contributions (Benson). The latter is the most accurate one. It also enables us to calculate the thermodynamic functions of radicals.

It is sometimes possible to employ a comparatively simple procedure—introduce a correction (or contribution) when going over from hydrocarbons to compounds containing oxygen, nitrogen, a halogen, or sulphur. The values of these corrections after Stull *et al.* [26] are also given in this appendix.

Section A1.5 presents simple equations found by the author that allow one to evaluate ΔH_f°, S°, C_p°, and $\log K_{p,f}^\circ$ for hydrocarbons for an arbitrary temperature and number of carbon atoms. These equations have been used on earlier pages to analyse groups of reactions of the type of alkane $\rightarrow$ alkene $+ H_2$, alkane $\rightarrow$ alkylbenzene $+ 4H_2$, and so on.

If it is necessary to find the thermodynamic functions of substances in the states of a real gas, liquid, or solid, the relations given in Chap. 2 can be used for the relevant conversions.

The heat of formation of a substance in the state of an ideal gas ΔH_f° is related to the heats of formation of the condensed substance $\Delta H_{f,\,cond}^\circ$, vaporization ΔH_v°, and of transition of the vapour to the

state of an ideal gas ΔH^* by the expression

$$\Delta H_f^\circ \approx \Delta H_{f,\,cond}^\circ + \Delta H_v^\circ + \Delta H^*$$

All the quantities must be taken for the same temperature. For example, for methanol, we have $\Delta H_{f,\,298}^\circ = -201.17$ kJ/mol, $\Delta H_{v,\,298}^\circ = 37.49$ kJ/mol, and $\Delta H^* = 0.9$ kJ/mol (calculated using Fig. 11). Hence, for liquid methanol, $\Delta H_{f,\,lq,\,298}^\circ \approx -201.17 - 37.49 - 0.9 = -239.56$ kJ/mol, which differs by only 1.0 kJ/mol from the experimentally found value [26].

The entropy of a substance in the state of an ideal gas S° is related to the entropy of the condensed substance S_{cond}°, the heat of vaporization ΔH_v°, and the saturated vapour pressure p_i° by the expression

$$S^\circ \approx S_{cond}^\circ + \frac{\Delta H_v^\circ}{T} + R \ln \frac{p_i^\circ}{p^\circ} + \frac{\Delta H^*}{T}$$

For methanol, we have $S_{293}^\circ = 239.7$ J/(mol·K), $\Delta H_{v,\,298}^\circ = 37.49$ kJ/mol, $p_i^\circ = 0.16p^\circ$, and $\Delta H^*/298 = 3.0$ J/mol. Therefore, the entropy of liquid methanol is

$$S_{lq,\,298}^\circ \approx 239.7 - \frac{37\,490}{298} - 8.31 \ln 0.16 - 3.0$$
$$= 239.7 - 125.80 + 15.23 - 3.0 = 126.1 \text{ J/(mol·K)}$$

which differs insignificantly from the value calculated by spectroscopic data [126.8 J/(mol·K)].

The Gibbs energies of formation of a gaseous ΔG_f° and condensed $\Delta G_{f,\,cond}^\circ$ substance are related as follows:

$$\Delta G_f^\circ \approx \Delta G_{f,\,cond}^\circ - RT \ln \frac{p_i^\circ}{p^\circ}$$

For methanol at 298 K, we have

$$\Delta G_{f,\,lq}^\circ \approx \Delta G_f^\circ + RT \ln \frac{p_i^\circ}{p^\circ} = -162.51 - 4.54 = -167.05 \text{ kJ}$$

which is close to the value of −166.5 kJ given in [26]. It is obvious that

$$\log K_{p,\,f,\,cond}^\circ \approx \log K_{p,\,f}^\circ - \log \left(\frac{p_i^\circ}{p^\circ}\right)$$

For methanol at 298 K, we have $\log K_{p,\,f}^\circ = 28.47$ and $\log K_{p,\,f,\,lq}^\circ = 28.47 - \log 0.16 = 29.27$, which is also close to the value of 29.12 given in [26].

Hence, it is not difficult to go over from the values of ΔH_f°, S°, ΔG_f°, and $\log K_{p,\,f}^\circ$ for the state of an ideal gas to the values of these quantities for a condensed state if we know the heats of vaporization, fusion, and the saturated vapour pressure of the relevant substance. This is why we shall consider the calculations of the thermodynamic functions of substances below only for the state of an ideal gas.

A 1.1. A Universal Empirical Method of Calculating the Standard Heats of Formation ΔH_f° Entropy S°, and Coefficients a, b, and c of the Temperature Dependence of the Heat Capacity ($C_p^\circ = a + bT + cT^2$) for Organic Compounds

In this method, corrections are introduced to the relevant thermodynamic function of the "parent" or "basic" substance. The basic substances include methane for acyclic compounds, cyclopentane for cyclic non-aromatic compounds, benzene for monocyclic aromatic compounds, naphthalene for dicyclic aromatic compounds, and methylamine for primary amines (Table A.1). The corrections are divided into the following types.

Table A.1. **Thermodynamic Properties of Basic Substances**

Substance	$\Delta H_{f,298}^\circ$, kJ/mol	Coefficients of equation $C_p^\circ = a + bT + cT^2$, J/(mol·K)			S_{298}°, J/(mol·K)
		a	$b\times10^3$	$c\times10^6$	
Methane	—74.9	14.08	73.51	—17.13	186.5
Cyclopentane	—77.4	10.79	340.47	—101.81	293.4
Benzene	82.8	0.95	220.54	—111.86	269.7
Naphthalene	150.8	12.97	450.55	—143.28	336.5
Methylamine	—23.1	16.56	126.52	—35.83	242.9
Dimethylamine	—18.9	16.14	198.96	—58.03	273.4
Trimethylamine	—24.0	16.19	271.20	—80.23	289.3
Dimethyl ether	—184.1	26.44	163.35	—47.16	267.5
Formamide	—207.1	26.80	103.70	—30.76	249.0

1. Primary corrections for the substitution of the hydrogen atom in the basic substance by a CH_3 group (Table A.2). Using these values, one can go over from methane to ethane, from cyclopentane to cyclohexane, methyl- or dimethyl cyclopentanes, from benzene and naphthalene to methyl- or dimethyl-substituted compounds, from methylamine to ethylamine, from dimethylamine to ethylmethylamine, and so on. For dimethyl ether, any substitution of hydrogen by CH_3 is considered to be a secondary one, and the relevant correction is absent in Table A.2.

2. Secondary corrections for the second, third, etc. substitution of a hydrogen atom by a CH_3 group. Two type numbers are taken into account when choosing these corrections, namely, of the carbon atom at which the substitution is being made (A) and of the neighbouring carbon atom (B). If carbon atom A is bound to several other carbon atoms, the one having the largest type number is chosen. The

type numbers (A or B) are chosen as follows depending on the number of hydrogen atoms bound to the carbon atom in the relevant group:

Group	CH_3	CH_2	CH	C	C in aromatic ring
Type number (A or B)	1	2	3	4	5

The secondary corrections for various combinations of A and B are given in Table A.3.

Table A.2. **Corrections for the Primary Substitution of Hydrogen by $-CH_3$ Groups**

Basic group	$\Delta(\Delta H^\circ_{f,\,298})$, kJ/mol	Coefficients of equation $C^\circ_p = f(T)$, J/(mol·K)			ΔS°_{298}, J/(mol·K)
		Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	
Methane	—9.2	—8.54	100.42	—40.46	43.5
Cyclopentane:					
growth of ring	—38.9	—4.35	80.75	—24.23	2.9
first substitution	—21.8	—0.29	77.70	—24.14	48.1
second substitution:					
ortho	—51.0	—1.00	194.81	—21.13	—
meta	—35.1				
para	—29.7				
third substitution	—29.3	—	—	—	—
Benzene and naphthalene:					
first substitution	—18.8	1.51	73.85	—24.60	50.2
second substitution:					
ortho	—26.4	21.76	25.19	4.94	33.9
meta	—27.2	7.20	59.33	—15.73	38.5
para	—33.5	5.36	60.96	—16.65	32.6
third substitution	—	2.38	69.12	—21.71	33.5
Methylamine	—23.8	—	—	—	—
Dimethylamine	—26.4	—0.42	73.30	—22.38	—
Trimethylamine	—17.2	—	—	—	—
Formamide	—37.7	25.56	—7.32	19.87	—

3. Corrections for the substitution of single carbon atom bonds by double or triple ones. The values of these corrections are given in Table A.4. When choosing them, one must take into account the type numbers of the carbon atoms where a single bond is being substituted.

4. Corrections for functional groups (C_6H_5, Cl, I, Br, CN, COOH, OH, NH_2, =O) substituting CH_3 groups (Table A.5). When an aldehyde group (=O) is being introduced, two CH_3 groups are substituted [for example, $CH_3CH(CH_3)_2 \rightarrow CH_3CHO$]. To illustrate the calculations using the universal method of corrections, let us consid-

Table A.3. **Corrections for Secondary Substitution of Hydrogen by $-CH_3$ Groups**

Type numbers (A)	Type numbers (B)	$\Delta(\Delta H^\circ_{f,298})$, kJ/mol	Coefficients of equation $C^\circ_p = f(T)$, J/(mol·K) Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, J/(mol·K)
1	1	—18.8	—4.06	95.65	—36.61	41.0
1	2	—21.8	4.64	77.28	—28.66	38.5
1	3	—23.0	4.18	83.18	—33.60	39.7
1	4	—20.9	5.82	71.63	—24.60	46.0
1	5	—25.5	0.42	71.88	—21.76	41.8
2	1	—27.6	7.91	73.64	—25.98	24.3
2	2	—28.5	6.36	83.47	—35.86	29.3
2	3	—28.5	4.23	82.38	—32.76	26.4
2	4	—21.3	10.54	67.40	—24.60	25.1
2	5	—24.3	0.04	72.89	—22.30	11.3
3	1	—33.9	—4.02	114.93	—51.80	11.3
3	2	—33.5	—4.98	120.37	—53.18	20.1
3	3	—28.9	—13.68	129.54	—58.83	24.3
3	4	—23.8	—0.59	102.80	—42.97	7.1
3	5	—38.5	1.76	67.78	—19.58	5.4
Substitution of hydrogen in ethers or esters		29.3	—0.04	73.55	—22.30	60.2
Substitution of hydrogen in acid with formation of ester		—39.7	1.84	69.58	—20.71	69.9

Table A.4. **Corrections for Substitution of Single Bonds by Double and Triple Ones**

Kind of bond between carbon atoms A and B	$\Delta(\Delta H^\circ_{f,298})$, kJ/mol	Coefficients of equation $C^\circ_p = f(T)$, J/(mol·K) Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS°_{298}, J/(mol·K)
1—1	137.2	5.56	—53.09	19.96	—8.8
1—2	125.5	6.53	—62.22	23.30	3.3
1—3	118.0	2.64	—98.95	54.81	9.2
2—2	117.2	1.67	—78.95	41.38	—3.8
2—2, *cis* position	118.8	1.67	—78.95	41.38	—2.5
2—2, *trans* position	115.1	1.67	—78.95	41.38	—5.0
2—3	111.7	2.64	—98.95	54.81	—6.7
3—3	106.7	—19.37	—74.64	49.71	
Additional correction for each pair of conjugate bonds	—15.9	Approximately 0			—43.5
1=1	311.3	23.35	—130.50	46.82	—28.5
1=2	289.1	26.86	—152.34	60.79	—32.6
2=2	272.4	19.50	—151.04	63.93	—26.4
Correction for double bond adjacent to aromatic ring	—21.3	Approximately 0			—18.0

er the determination of the heat of formation of benzaldehyde and the entropy of 3-chloro-1-propene.

Benzaldehyde can be prepared by using benzene as the basic substance, next substituting H by CH_3 up to the formation of iso-

Table A.5. **Corrections for Groups Substituting the $-CH_3$ Group**

Group	$\Delta(\Delta H^\circ_{f,298})$, kJ/mol	Coefficients of equation $C^\circ_p = f(T)$, J/(mol·K)			ΔS°_{298}, J/(mol·K)
		Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	
—Br	41.8	11.76	—81.21	26.48	12.6
—CN	163.2	15.23	—58.24	18.95	16.7
—COOH	—364.0	35.56	—63.05	33.22	64.4
$-C_6H_5$	135.1	—3.31	224.39	—80.37	90.8
—Cl	0 for the first Cl atom at C; 18.8 for each following one	9.16	—78.87	26.19	0
—F	—146.4	9.37	—98.78	49.33	—4.2
—I	103.8	11.42	—72.68	17.11	20.9
$-NH_2$	51.5	5.27	—30.63	9.33	—20.1
$-NO_2$	5.0	26.36	—81.71	43.35	8.4
=O (aldehyde)	—54.0	15.10	—233.13	95.06	—51.5
—O (ketone)	—55.2	21.0	—276.48	126.40	—10.0
—OH (aliphatic and aromatic in *meta*- and *para*-position)	—136.8	13.26	—62.17	23.39	10.9
—OH (aromatic in *ortho*-position)	—199.6				
—SH	66.1	17.03	—104.43	51.76	21.8

propylbenzene, and substituting two CH_3 groups in the latter by oxygen. The calculations are performed by the following scheme:

$$\underset{\Delta H^\circ_f = 82.8}{C_6H_6} \xrightarrow[-18.8]{\text{primary substitution}} \underset{-25.5}{C_6H_5CH_3} \xrightarrow{\text{secondary substitution, A=1, B=5}}$$

$$\rightarrow C_6H_5CH_2CH_3 \xrightarrow[-24.3]{\text{secondary substitution, A=2, B=5}} C_6H_5CH(CH_3)_2 \xrightarrow[-54.0]{\text{functional substitution of } =(CH_3)_2 \text{ by } =O}$$

$$\rightarrow C_6H_5CHO$$
$$= -39.8 \text{ kJ/mol}$$

The calculations for 3-chloro-1-propene are performed as follows:

$$\underset{S^\circ_{298}=186.5}{CH_4} \xrightarrow[+43.5]{\text{primary substitution}} CH_3CH_3 \xrightarrow[+41.0]{\text{secondary substitution, A=1, B=1}}$$

$$\rightarrow CH_3CH_2CH_3 \xrightarrow[+38.5]{\text{secondary substitution, A=1, B=2}} CH_3CH_2CH_2CH_3 \rightarrow$$

$$\xrightarrow[+3.3]{\text{substitution of single bond by double one, A=1, B=2}} CH_2{=}CH{-}CH_2CH_3 \xrightarrow[+0]{\text{functional substitution of } CH_3 \text{ by Cl}}$$

$$\rightarrow \underset{=312.8\ J/(mol\cdot K)}{CH_2{=}CH{-}CH_2Cl}$$

These values differ from published ones by not over 1.5%.

When using the method of corrections (contributions), one can begin the calculations by choosing any substance as the basic one (not necessarily one indicated in Table A.1). For example, the heat of formation of benzaldehyde can be found from that of isopropylbenzene and the correction for the substitution of two CH_3 groups by $=O$. This expands the possibilities of the method quite substantially if standard thermodynamic tables are available. Thus, initially, the universal method of corrections does not allow one to determine the thermodynamic functions for *cis*- or *trans*-alkenes. But if we combine it with the method of corrections for alkenes, we shall be able to determine the thermodynamic functions for various alkenes and their derivatives. If, for example, it is necessary to find the thermodynamic functions for the unsaturated acid $CH_3CH{=}CH{-}CH_2CH_2COOH$ (the *cis*-form), one can use *cis*-2-pentene as the basic substance and then the universal method of corrections:

$$cis\text{-}CH_3{-}CH{=}CH{-}CH_3 \xrightarrow{\text{secondary substitution}}$$

$$\rightarrow cis\text{-}CH_3CH{=}CH{-}CH_2{-}CH_2{-}CH_3 \xrightarrow{\text{functional substitution}}$$

$$\rightarrow cis\text{-}CH_3CH{=}CH{-}CH_2{-}CH_2COOH$$

This will yield the required value.

A1.2. Calculation of the Thermodynamic Properties of Organic Compounds by the Additivity Rule (Benson's Method)

Attempts were repeatedly made to calculate the thermodynamic functions of organic compounds by summing the contributions of the component groups whose number is relatively small. For example,

to calculate ΔH_f° of primary *n*-decyl alcohol, it seemed alluring to sum the contributions from the group $-CH_3$, eight groups $-CH_2$, and the group $-CH_2OH$. A method using such additivity was proposed by Remolo Ceola and is described in [4]. The accumulation of accurate data and the introduction of corrections made it possible to improve the additivity rule. To date, Benson's method [69-71] is the most refined one.

This method takes into account the contributions of the constituent groups to the values of ΔH_f°, S°, and C_p° for molecules of organic compounds and, as indicated by Benson and Buss [69], yields for hydrocarbons, on the average, an error in the value of ΔH_f° of not over 4 kJ/mol and in the values of S° and C_p° of not over 4 J/(mol·K). These values are commensurable with the errors of measurement.

The method is based on the fact that when two molecules ABA and CBC, where A, B, and C are atoms or groups, enter into a disproportionation reaction, i.e.

$$ABA + CBC \rightarrow 2ABC$$

the change in a thermodynamic function Φ of the system is related only to a change in the symmetry.

Indeed, for example, the heat of the reaction ΔH can be calculated by the difference in the binding energies in the initial and final states. For the above reaction

$$\Delta H = (2E_{A-B} + 2E_{C-B})_{in} - (2E_{A-B} + 2E_{C-B})_{fin}$$

If the binding energies E_{A-B} and E_{C-B} do not depend on the nature of the second substituent, $\Delta H = 0$. The latter statement holds to a first approximation when A and C are substantial fragments of a molecule commensurable with it in size.

This conclusion can also be generalized for the asymmetrical molecules ABB′A and CBB′C that enter into the reaction

$$ABB'A + CBB'C \rightarrow ABB'C + CBB'A$$

For the two kinds of disproportionation reactions indicated above, we assume that $\Delta H = 0$, $\Delta C_p = 0$, and $\Delta S = R \ln \sigma$, where σ is the symmetry number.

It follows from the above that a thermodynamic function Φ of a molecule can be calculated from the values of Φ for the fragments of this molecule.

The possibility of calculating ΔH°, S°, and C_p° from data for atoms or bonds was studied [69], but such calculations were found to result in appreciable errors. The best coincidence was obtained when calculating ΔH°, S°, and C_p° from data on the contributions to these quantities of the constituent groups that can participate in the disproportionation reactions.

In Benson's method, the thermodynamic quantities are determined for the groups forming a molecule. Benson *et al.* define a group to be the central atom together with the ligands. For example, a carbon atom bound to three hydrogen atoms and one carbon atom is defined to be a group and is designated as $C—(H)_3(C)$. Benson *et al.* [69, 70] determined the contributions to ΔH_f°, S°, and C_p°, for example, for the following groups:

Compound	Constituent groups
Alkanes —C—C—	$C—(C)_2(H)_2$; $C—(C)_3(H)$; $C—(C)(H)_3$; $C—(C_4)$; steric corrections are taken into account
Alkenes $—C_d=C_d—$	$C_d—(H)_2$; $C_d—(C)(H)$; $C_d—(C)_2$; $C—(C_d)(C)(H)_2$; $C—(C_d)(C)(H)_3$; $C—(C_d)(C)_3$; steric corrections and corrections for a *cis*-configuration are taken into account
Dienes	$C_d—(C_d)(H)$; $C_d—(C_d)(C)$; $C—(C_d)_2(H)_2$; C_a (the first carbon atom in an allene group)
Acetylenes $—C_t\equiv C_t—$	$C_t—(H)$; $C_t—(C)$; $C—(C_t)(C)(H)_2$; $C—(C_t)(C)_2(H)$; $C_t—(C_d)$; $C_d—(C_t)(H)$
Alkylbenzenes	$C_b—(H)$; $C_b—(C)$; $(C—C_b)(C)(H)_2$; $C—(C_b)(C)_2(H)$; $C—(C_b)(C)_3$; a correction for the *ortho*-position is taken into account
Unsaturated alkylbenzenes	$C_b—(C_d)$; $C_d—(C_b)(H)$; $C_d—(C_b)(C)$; $C_b—(C_t)$; $C_t—(C_b)$
Polycyclic aromatic compounds	a correction for the group $C_b—(C_b)$ is taken into account
Cyclic alkanes and alkenes	a correction for the ring and corrections for the structure are taken into account

Benson and Buss [69] also determined the thermodynamic functions of the constituent groups for oxygen-, nitrogen-, halogen-, sulphur-, boron-, and metal-containing compounds. The values of these functions are given in Table A.6. They found, however, that corrections sometimes have to be introduced when calculating the values of ΔH°, S°, and C_p°. Cases when such corrections are required are characterized in Table A.7.

For example, when calculating ΔH_f° for 2-methylbutane, one correction is introduced for branching, for 2,3-dimethylbutane two corrections for branching are introduced, and so on.

The following rules must be observed when calculating thermodynamic functions by Benson's method.

1. The values of the thermodynamic functions can be calculated for any temperature by the expressions:

$$\Delta H_T^\circ = \Delta H_{300}^\circ + \overline{\Delta C_p^\circ}\,(T - 300)$$

$$\Delta S_T^\circ = \Delta S_{300}^\circ + \overline{\Delta C_p^\circ} \ln\left(\frac{T}{300}\right)$$

where $\overline{\Delta C_p^\circ} = 0.5\,(\overline{\Delta C_{p,T}^\circ} + \Delta C_{p,300}^\circ)$.

Table A.6. **Thermodynamic Functions for Constituent Groups and Corrections**

Groups	ΔH°_f, kJ/mol	S°, J/(mol·K)	C°_p, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
Hydrocarbon Groups									
$C-(H)_3(C)$	−42.17	127.2	25.9	32.8	39.33	45.15	54.48	61.80	73.55
$C-(H)_2(C)_2$	−20.71	39.41	23.01	29.08	34.52	39.12	46.32	51.63	59.62
$C-(H)(C)_3$	−7.95	50.5	19.0	25.10	30.0	33.68	38.95	42.05	46.74
$C-(C)_4$	2.09	−146.86	18.28	25.65	30.79	33.97	36.69	36.65	33.97
$C_d-(H)_2$	26.19	115.52	21.34	26.61	31.42	35.56	42.13	47.15	55.19
$C_d-(H)(C)$	35.94	33.35	17.41	21.05	24.31	27.20	32.01	35.35	40.25
$C_d-(C)_2$	43.26	−53.14	17.15	19.29	20.88	22.01	24.27	25.44	26.61
$C_d-(C_d)(H)$	28.37	26.69	18.66	24.23	28.24	31.05	34.94	37.61	41.76
$C_d-(C_d)(C)$	37.15	−61.09	18.41	22.47	24.81	25.86	27.20	27.70	28.12
$C_d-(C_b)(H)$	28.37	26.69	18.66	24.23	28.24	31.05	34.94	37.61	41.76
$C_d-(C_b)(C)$	36.15	−61.09	18.41	22.47	24.81	25.86	27.20	27.70	28.12
$C_d-(C_b)_2$	19.25								
$C_d-(C_b)_2$	33.47								
$C_d-(C_t)(H)$	28.37	26.77	18.66	24.22	28.24	31.05	34.94	37.61	41.76
$C_d-(C_t)(C)$	35.69	—	18.41	22.47	24.81	25.86	27.20	27.70	—
$C-(C_d)(H)_3$	−42.17	127.23	25.90	32.80	39.33	45.14	54.47	61.80	—
$C-(C_d)(C)(H)_2$	−19.92	41.0	21.42	28.70	34.81	39.71	46.94	52.22	60.08
$C-(C_d)_2(H)_2$	−17.95	42.68	19.67	28.45	35.15	40.17	47.28	52.72	60.25
$C-(C_d)_2(C)_2$	4.85	—	14.94	25.02	31.42	35.02	37.66	37.74	—
$C-(C_d)(C)_3$	7.03	−145.27	16.69	25.27	31.09	34.56	37.32	37.49	34.43
$C-(C_d)(C_b)(H)_2$	−17.95	42.68	19.67	28.45	35.15	40.17	47.28	52.78	60.25
$C-(C_t)(C)(H)_2$	−19.79	43.10	20.71	27.45	33.18	37.99	45.44	51.00	59.41
$C-(C_b)(C)(H)_2$	−20.33	38.91	24.43	31.84	37.57	41.88	48.07	52.47	57.57
$C-(C_d)_2(C)(H)$	−5.19	—	15.65	24.48	30.63	34.73	39.92	39.91	43.14
$C-(C_d)(C)_2(H)$	−6.19	−48.95	17.41	24.73	30.71	34.27	39.58	42.63	47.20
$C-(C_t)(H)_3$	−42.17	127.23	25.90	32.80	39.33	45.14	54.47	61.80	—
$C-(C_t)(C)_2(H)$	−7.20	−46.86	16.69	23.47	28.66	32.55	38.07	41.42	46.53
$C-(C_b)(H)_3$	−42.17	127.23	25.90	32.80	39.33	45.14	54.47	61.80	—

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T; K						
			300	400	500	600	800	1000	1500
$C-(C_b)(C)(H)_2$	−20.33	38.91	24.43	31.84	37.57	41.88	48.07	52.47	—
$C-(C_b)(C)_2(H)$	−4.10	−51.04	20.42	27.87	33.05	36.61	40.71	42.89	44.69
$C-(C_b)_2(C)(H)$	−5.19	—	15.65	24.48	30.63	34.73	39.91	43.14	—
$C-(C_b)_2(C)_2$	4.85	—	14.94	25.02	31.42	35.02	37.66	37.74	—
$C-(C_b)(C_d)(H)_2$	−17.95	42.68	19.66	28.45	35.14	40.17	47.28	52.72	—
$C-(C_b)(C)_3$	11.76	−147.19	18.28	28.41	33.85	36.74	38.45	37.49	31.91
$C_t-(H)$	112.68	103.34	22.05	25.06	27.15	28.74	31.25	33.30	37.03
$C_t-(C)$	115.27	26.57	13.10	14.56	15.94	17.11	19.25	20.59	26.57
$C_t-(C_d)$	122.17	26.90	10.75	14.81	14.64	20.58	22.34	23.01	24.27
$C_t-(C_b)$	122.17	26.90	10.75	14.81	14.64	20.58	22.34	23.01	24.27
$C_b-(H)$	13.81	48.24	13.57	18.58	22.84	26.36	31.55	35.19	40.71
$C_b-(C)$	23.05	−32.17	11.17	13.14	15.40	17.36	20.75	22.76	25.02
$C_b-(C_d)$	23.77	−32.64	15.02	16.61	18.33	19.75	22.09	23.47	24.06
$C_b-(C_t)$	23.77	−32.64	15.02	16.61	18.33	19.75	22.09	23.47	24.06
C_b-C_b	20.75	−36.15	13.93	17.66	20.46	22.05	24.10	24.90	25.31
C_a (allene)	143.09	25.10	16.32	18.41	19.66	20.92	22.18	23.01	23.85
Corrections for Neighbouring Hydrocarbon Groups									
gauche (alkanes)	3.35								
gauche (alkenes)	2.09								
cis	4.18	*	−5.6	−4.6	−3.4	−2.6	−1.6	−1.1	0
ortho	2.38	−6.74	4.69	5.65	5.44	4.89	3.68	2.76	0.21
Corrections for Cyclic Compounds									
Ring (σ)									
Cyclopropane (6)	115.48	134.31	−12.76	−10.59	−8.79	−7.95	−7.41	−6.78	—
Cyclopropene (2)	224.68	140.58	—	—	—	—	—	—	—
Cyclobutane (8)	109.62	124.68	−19.29	−16.28	−13.14	−11.05	−7.87	−5.77	—
Cyclobutene (2)	124.68	121.33	−10.59	−9.16	−7.91	−7.03	−6.19	−5.56	—

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
Cyclopentane (10)	26.36	114.22	−27.20	−23.01	−18.83	−15.90	−11.72	−7.95	—
Cyclopentene (2)	24.69	107.95	−25.02	−22.38	−20.46	−17.32	−12.26	−9.46	—
Cyclopentadiene	25.10	117.15	−17.99	—	—	—	—	—	—
Cyclohexane (6)	0	78.66	−24.27	−17.15	−12.13	−5.44	4.60	9.20	—
Cyclohexene (2)	5.86	89.96	−17.91	−12.72	−8.28	−5.98	−1.21	−0.33	—
Cyclopentane (1)	26.78	66.53	—	—	—	—	—	—	—
Cyclooctane (8)	41.42	69.04	—	—	—	—	—	—	—
Naphthalene	—	33.89	—	—	—	—	—	—	—
Cyclooctatetraene	71.55								
Cyclononane	53.55								
cis-Cyclononene	41.42								
trans-Cyclononene	53.55								
Spiropentane	265.68	282.83							
Dicyclo(1,1,0)-butane	280.33	289.53							
Dicyclo(2,1,0)-pentane	231.37								
Dicyclo(3,1,0)-hexane	136.82								
Dicyclo(4,1,0)-heptane	120.92								
Dicyclo(5,1,0)-octane	123.85								
Dicyclo(6,1,0)-nonane	130.12								
Oxygen-Containing Groups									
CO−(CO)(C)	−122.17		22.48	26.44	29.96	32.93	37.66	40.84	
CO−(O)(C_d)	−135.98		24.98	28.03	31.00	33.56	37.11	39.16	
CO−(O)(C_b)	−135.98		9.12	11.5	16.65	21.05	26.32	29.54	
CO−(CO)(H)	−108.78		28.12	32.76	37.24	41.38	47.28	50.71	
CO−(O)(C)	−146.86	20	24.98	28.03	30.96	33.56	37.11	39.16	
CO−(O)(H)	−134.31	146.15	29.41	32.93	36.9	40.5	46.69	51.04	
CO−(C_d)(H)	−132.63		29.41	32.93	36.9	40.5	46.69	52.04	
CO−$(C_b)_2$	−159.41		22.0	28.33	32.08	35.48	40.25	41.21	

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
CO−(C_b)C	−129.29		23.77	28.95	32.22	34.98	39.29	40.84	
CO−(C_b)H	−144.77		26.78	32.3	37.28	41.21	48.07	50.58	
CO(C)$_2$	−131.38	62.80	23.39	26.44	29.66	32.47	37.2	40.21	
CO−(C)(H)	−121.75	146.15	29.41	32.93	36.9	40.5	46.69	51.04	
CO−(H)$_2$	−108.78	224.56	35.44	39.25	43.76	48.2	55.94	61.97	
CO−(C_b)(CO)	−135.98		8.62	11.3	13.01	14.31	16.23	17.49	
O−(CO)$_2$	−212.97		−1.72	7.45	13.39	16.74	21.46	28.48	
O−(CO)(O)	−79.50		15.48	15.48	15.48	15.48	17.57	17.57	
O−(CO)(C_d)	−196.23		6.02	12.47	16.65	18.79	20.79	21.76	
O−(CO)(C)	−185.35	35.1	16.32	15.1	17.53	19.33	20.88	20.17	
O−(CO)(H)	−243.09	102.59	15.94	20.84	24.27	26.53	30.08	32.43	
O−(O)(C)	−18.83	39.33	15.48	15.48	15.48	15.48	17.57	17.57	
O−(O)$_2$	−79.50	39.33	15.48	15.48	15.48	15.48	17.57	17.57	
O−(O)(H)	−68.07	116.52	21.63	24.23	26.28	27.87	29.92	31.42	
O−(C_d)$_2$	−137.24	42.26	14.23	15.48	15.48	15.9	18.41	19.25	
O−(C_d)(C)	−133.47	40.58	14.23	15.48	15.48	15.9	18.41	19.25	
O−(C_b)$_2$	88.28		4.56	5.10	6.28	8.33	11.92	14.69	
O−(C_b)C	−94.56		14.23	15.48	15.48	15.9	18.41	19.25	
O−(C_b)(H)	−158.57	121.71	17.99	18.83	20.08	21.76	25.1	27.61	
O−(C)$_2$	−99.16	36.32	14.23	15.48	15.48	15.9	18.41	19.25	
O−(C)(H)	−158.57	121.63	18.12	18.62	20.17	21.88	25.19	27.66	
C_d−(CO)(O)	37.66		23.39	29.29	31.3	32.43	33.56	34.02	
C_d−(CO)C	39.33		15.61	18.74	21	22.59	24.98	26.65	
C_d−(CO)(H)	35.56		15.86	20.5	24.43	27.78	32.64	36.57	
C_d−(O)(C_d)	37.24		18.41	22.47	24.81	25.86	27.2	27.7	
C_d−(O)(C)	43.1		17.15	19.29	20.88	22.01	24.27	25.44	
C_d−(O)(H)	35.98		17.41	21.05	24.31	27.2	32.01	35.35	
C_b−(CO)	40.58		11.17	13.14	15.4	17.36	20.75	22.76	
C_b−(O)	−3.77	−42.68	16.32	22.18	25.94	27.61	28.87	28.87	

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
$C-(CO)_2(H)_2$	−31.8		23.43	29.5	35.1	40.5	48.45	53.85	
$C-(CO)(C)_2(H)$	−7.5	−50.21	25.98	31.63	33.47	34.35	38.41	40.29	
$C-(CO)(C)(H)_2$	−21.76	40.17	25.94	32.22	36.4	39.75	46.44	51.04	
$C-(CO)(C)_3$	6.69		21.21	28.79	32.68	34.6	36.82	36.07	
$C-(CO)(H)_3$	−42.26	127.24	25.9	32.8	39.33	45.15	54.48	61.8	
$C-(O)_2(C)_2$	−77.8		6.65	16.53	25.94	30.92	31.88	35.48	
$C-(O)_2(C)(H)$	−68.2		21.17	30.46	37.78	39.37	43.14	44.98	
$C-(O)_2(H)_2$	−63.18		11.84	21.17	31.46	38.16	43.18	47.24	
$C-(O)(C_b)(H)_2$	−33.89	40.58	15.52	26.23	34.64	40.96	49.33	55.23	
$C-(O)(C_b)(C)(H)$	−25.44		21.51	30.54	36.94	39.46	42.8	44.35	
$C-(O)(C_d)(H)_2$	−28.87		19.5	29.16	36.19	41.34	48.28	53.26	
$C-(O)(C)_3$	−27.6	−140.42	18.12	25.9	30.33	32.22	34.31	34.48	
$C-(O)(C)_2(H)$	−30.12	−46.02	20.08	27.78	33.89	36.53	41.05	43.51	
$C-(O)(C)(H)_2$	−33.89	41	20.88	28.66	34.73	39.46	46.48	51.59	
$C-(O)(H)_3$	−42.26	127.24	25.9	32.8	39.33	45.15	54.52	61.8	
Corrections for Stressed Structure or Ring									
Oxygen of ether (*gauche*)	1.26		−0.42	−3.72	−4.6	−3.05	−2.51	−0.96	
Ditertiary esters	32.64		−16.48	−23.6	−29.92	−36.94	−50.38	−62.34	
Ethylene oxide	115.48	131.38	−0.368	−11.71	−12.55	−10.88	−9.62	−9.62	
Trimethylene oxide	110.46	115.90	−19.25	−20.92	−17.57	−14.64	−10.88	0.84	
Tetrahydrofuran	28.03		−17.78	−18.99	−17.03	−14.85	−12.93	−10.92	
Tetrahydropyran	9.20		−17.91	−12.72	−8.28	−5.98	−1.21	0.33	
1,3-Dioxan	3.76		−10.50	−12.05	−9.54	−6.23	−10.9	2.34	
1,4-Dioxan	22.59		−17.40	−19.12	−13.01	−7.86	−4.56	−1.97	
1,3,5-Trioxan	21.34		7.49	2.34	−2.55	−2.72	−5.02	−10.17	
Furan	−24.27		−17.53	−15.19	−12.22	−10.00	−8.33	−7.20	
Dihydropyran	5.02		−18.58	−13.39	−6.53	−1.88	1.76	2.76	
Cyclopentanone	21.76		−35.69	−30.08	−22.22	−15.56	−9.45	−5.10	

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
Cyclohexanone	9.20		−33.89	−27.49	−17.74	−7.99	2.93	8.24	
Succinic anhydride	18.83		−33.05	−25.19	−18.79	−14.98	−14.02	−12.80	
Glutaric anhydride	3.35		−33.18	−25.27	−18.83	−15.02	−14.02	−12.84	
Maleic anhydride	15.06		−21.42	−14.14	−8.45	−9.16	−1.55	−0.04	
Nitrogen-Containing Groups **									
C−(N)(H)$_3$	−42.17	127.43	25.90	32.80	39.33	45.14	54.47	60.54	73.55
C−(N)(C)(H)$_2$	−27.61	41.0	21.97	28.87	34.64	39.29	46.40	51.63	—
C−(N)(C)$_2$(H)	−21.76	−48.95	19.54	26.44	31.96	35.10	40.00	42.80	—
C−(N)(C)$_3$	−13.39	−142.67	18.20	25.77	30.58	33.09	35.52	35.56	—
C−(N$_a$)(C)(H)$_2$	−23.01	41.00							
C−(N$_a$)(C)$_2$(H)	−13.81	48.95							
C−(N$_a$)(C)$_3$	−7.95	−145.18							
N−(C)(H)$_2$	20.08	124.31	23.93	27.24	30.63	33.76	39.37	43.81	51.38
N−(C)$_2$(H)	64.43	37.40	17.57	21.80	25.65	28.58	33.05	36.19	39.98
N−(C)$_3$	102.09	−56.32	14.56	19.08	22.72	24.98	27.45	27.91	27.20
N−(N)(H)$_2$	47.70	121.88	25.52	30.88	35.27	38.78	44.1	48.2	55.19
N−(N)(C)(H)	87.44	40.22	20.17	24.27	27.20	29.29	32.63	34.73	37.66
N−(N)(C)$_2$	122.17	−57.74	6.53	10.46	13.85	16.19	19.33	20.88	
N−(N)(C$_b$)(H)	92.47		13.72	16.94	19.87	22.22	26.27	28.91	
N$_I$−(C)	89.12		10.38	13.97	16.53	17.95	19.20	19.25	
N$_I$−(C$_b$)	69.87		10.38	13.47	15.94	17.66	20.04	21.42	
N$_a$−(H)	105.02	112.13	18.32	20.46	22.76	24.85	28.32	31.04	35.31
N$_a$−(C)	135.98	33.47	11.30	17.15	20.58	22.34	23.81	23.89	
N−(C$_b$)(H)$_2$	20.08	124.31	23.93	27.24	30.63	33.76	39.37	43.81	51.38
N$_I$−(H)	68.20	51.46	12.34	19.16	26.99	22.26	38.20	41.50	
N−(C$_b$)(C)(H)	62.34		15.98	20.46	23.89	26.27	30.08	32.34	
N−(C$_b$)(C)$_2$	109.62		2.59	8.45	13.68	17.28	21.88	23.39	
N−(C$_b$)$_2$(H)	68.20		9.04	13.05	17.28	21.34	28.28	32.97	

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
$C_b-(N)$	−2.09	−40.54	16.53	21.80	24.85	26.44	27.32	27.44	—
$N_a-(N)$	96.23		8.87	17.49	23.05	28.32	28.70	29.50	
$CO-(N)(H)$	123.85	146.15	29.41	32.93	36.90	40.5	48.53	51.04	—
$CO-(N)(C)$	−137.23	67.78	22.47	25.81	29.58	32.05	40.25	46.82	—
$N-(CO)(H)_2$	−62.34	103.30	17.03	24.02	29.83	34.68	41.67	46.86	—
$N-(CO)(C)(H)$	−18.41	16.32	16.19	21.25	24.89	28.28	28.74	27.36	
$N-(CO)(C_b)(H)$	1.67		12.68	16.36	19.25	23.35	26.07	26.44	
$N-(CO)_2(H)$	−77.40		15.02	23.18	28.03	30.92	93.26	34.27	
$N-(CO)_2(C)$	−24.68		4.48	12.97	18.03	20.92	22.93	27.07	
$N-(CO)_2(C_b)$	−2.09		4.10	12.80	17.70	20.29	22.09	22.13	
$C-(CN)(C)(H)_2$	94.14	168.20	46.44	56.06	64.85	71.96	82.42	89.12	
$C-(CN)(C)_2(H)$	107.95	82.84	46.02	53.14	58.99	64.43	72.38	77.82	
$C-(CN)(C)_3$	121.34	−11.71	36.19	46.69	53.93	58.78	64.89	67.74	
$C-(CN)_2(C)_2$		118.82	61.59	74.43	83.68	90.42	99.49	104.43	
$C_d-(CN)(H)$	156.48	153.05	41.00	48.95	55.65	60.67	68.20	72.38	
$C_d-(CN)_2$	351.87		56.90	62.24	78.16	84.73	93.47	98.70	
$C_d-(NO_2)(H)$	—	185.77	51.46	63.18	72.80	80.33	90.37	97.07	105.85
$N-(CO)(C)_2$	19.66		7.66	15.86	21.92	25.90	29.75	114.72	
$C_d-(CN)(C)$	163.80	66.57	40.75	47.20	52.22	55.48	60.46	62.47	
$C_b-(CN)$	149.79	85.77	41.00	46.86	51.46	54.81	59.41	62.34	—
$C_t-(CN)$	266.94	148.11	43.09	47.28	50.63	53.14	56.90	59.83	64.01
$C-(NO_2)(C)(H)_2$	−63.18	202.50	56.86	66.19	77.49	86.44	99.54	108.36	
$C-(NO_2)(C)_2(H)$	−66.11	112.55	50.17	63.54	74.14	82.05	92.80	99.16	
$C-(NO_2)(C)_3$	—	16.32	41.38	55.81	66.36	73.72	81.21	87.28	
$C-(NO_2)_2(C)(H)$	−62.34		72.47	95.48	113.26	126.40	143.72	154.10	
$O-(NO)(C)$	−24.68	175.31	38.07	43.09	46.86	50.21	55.65	58.16	60.67
$O-(NO_2)(C)$	−81.17	202.92	39.91	48.28	55.48	65.27	53.57	72.72	

Table A.6 (*continued*)

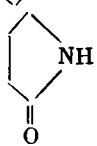
Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
Corrections for the Presence of a Ring in Nitrogen-Containing Compounds									
Ethyleneimine	115.90	132.21	−8.66	−9.12	−9.08	−8.58	−8.12	−7.86	
Azetidine	109.62	122.59	−19.79	−18.91	−17.07	−29.66	−11.18	0.04	
Pyrrolidine	28.45	111.71	−25.81	−23.35	−20.08	−16.74	−12.01	−9.08	
Piperidine	4.184		−2.34	1.55	4.52	6.53	7.15	−1.92	
Succinimide 	35.56		9.04	17.07	25.69	33.51	38.12	40.88	
Approximate Group Contribution $\Delta H_{f,298}^\circ$. Mixed Groups									
$N-(NO_2)(C)_2$	74.47								
$C-(N)_3(C)(H)_2$	292.88								
$N-(N)(C_b)_2$	151.88								
N_1-N_1	90.37								
N_1-C_b	58.99								

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
C_b-N_1	−2.09								
C−(NO)(C)(H)$_2$	79.91								
C−(NO)(C)$_2$(H)	92.88								
C−(NO)(C)$_3$	97.07								
N−(O)(H)$_2$	20.08								
N−(O)(C)(H)	51.04								
O−(N)(H)	−58.99								
O−(N)(C)	−3.76								
N_1−(OH)	−20.92								
C−(N)$_2$(H)$_2$	−50.63								
Halogen-Containing Groups									
C−(F)$_3$(C)	−662.75	177.82	53.14	62.76	68.62	74.89	80.75	83.68	—
C−(F)$_2$(H)(C)	−457.31	163.59	41.42	50.21	57.32	63.18	69.87	74.48	—
C−(F)(H)$_2$(C)	−215.48	148.11	33.89	41.84	50.21	54.39	63.60	69.45	—
C−(F)$_2$(C)$_2$	−405.85	74.48	41.42	49.37	56.48	60.25	67.36	69.45	—
C−(F)(H)(C)$_2$	−205.02	58.58	30.54	37.82	43.81	48.37	54.81	58.62	—
C−(F)(C)$_3$	−202.92	—	28.45	37.07	42.68	46.69	52.01	53.22	—
C−(F)$_2$(Cl)(C)	−444.76	169.45	57.32	67.36	73.22	77.82	82.84	85.35	—
C−(Cl)$_3$(C)	−86.61	210.87	68.20	75.31	79.91	82.84	86.19	87.86	—
C−(Cl)$_2$(H)(C)	(−79.08)	182.84	50.63	58.58	64.43	69.04	74.89	78.24	—
C−(Cl)(H)$_2$(C)	−69.04	158.16	37.24	44.77	51.46	56.07	64.02	69.87	—
C−(Cl)$_2$(C)$_2$	−92.05	93.72	51.04	62.26	66.73	68.95	70.96	71.21	—
C−(Cl)(H)(C)$_2$	−61.92	73.64	37.66	41.42	43.93	46.86	58.16	61.09	—
C−(Cl)(C)$_3$	−53.56	−22.59	38.91	43.93	46.02	47.28	51.88	53.14	—
C−(Br)$_3$(C)	—	233.05	69.87	75.31	78.66	81.17	83.26	84.94	—
C−(Br)(H)$_2$(C)	−22.59	170.71	38.07	46.02	52.72	57.32	64.85	70.29	—
C−(Br)(H)(C)$_2$	−14.23	—	37.36	44.60	50.04	53.72	58.79	61.59	—
C−(Br)(C)$_3$	−1.67	−8.37	38.91	46.02	48.12	51.46	55.65	55.65	—

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
C−(I)(H)$_2$(C)	33.47	179.91	38.49	46.02	53.97	58.16	66.11	71.96	—
C−(I)(H)(C)$_2$	49.93	89.12	38.49	45.61	51.04	54.39	59.41	61.92	—
C−(I)(C)(C$_d$)(H)	55.73	—	34.02	41.92	49.45	52.72	58.58	62.34	—
C−(I)(C$_d$)(H)$_2$	34.27	—	36.90	45.65	54.27	58.74	66.73	72.55	—
C−(I)(C)$_3$	54.39	0	41.13	49.16	54.06	56.27	57.70	56.90	—
C−(Cl)(Br)(H)(C)	—	191.21	51.88	58.58	65.27	68.20	74.89	79.50	—
N−(F)$_2$(C)	−32.64	—	34.52	42.38	48.20	53.56	60.12	62.68	—
C−(Cl)(C)(O))(H)	−90.37	62.76	41.21	43.56	46.23	48.41	52.09	54.98	—
C−(I)$_2$(C)(H)	(108.78)	(228.45)	53.09	61.84	67.82	71.63	76.61	79.62	—
C−(I)(O)(H)$_2$	15.90	170.29	34.39	43.89	51.17	56.69	64.22	69.33	—
C$_d$−(F)$_2$	−324.26	156.06	40.58	46.02	50.21	53.14	57.74	60.67	—
C$_d$−(Cl)$_2$	−7.53	176.16	47.70	52.3	55.65	58.16	61.09	62.76	—
C$_d$−(Br)$_2$	—	199.16	51.46	55.23	58.16	59.83	62.34	63.60	—
C$_d$−(F)(Cl)	—	166.52	43.10	48.95	52.72	55.65	59.41	61.50	—
C$_d$−(F)(Br)	—	177.82	45.19	50.21	53.56	56.48	59.83	61.50	—
C$_d$−(Cl)(Br)	—	188.70	50.63	53.14	56.48	58.99	61.50	61.50	—
C$_d$−(F)(H)	−157.32	137.24	28.45	35.15	39.75	43.93	49.37	53.14	—
C$_d$−(Cl)(H)	−5.02	148.11	33.05	38.49	43.10	46.86	51.46	54.81	—
C$_d$−(Br)(H)	46.02	160.25	33.89	39.75	44.35	47.70	51.88	55.23	—
C$_d$−(I)(H)	102.51	169.45	36.82	41.84	45.61	48.53	52.72	55.65	—
C$_d$−(C)(Cl)	−8.79	62.76	33.47	35.15	35.56	37.66	38.49	39.33	—
C$_d$−(C)(I)	98.74	—	37.24	38.49	38.07	39.33	39.75	40.17	—
C$_d$−(C$_d$)(Cl)	−14.90	—	34.73	38.49	39.33	41.42	41.42	41.42	—
C$_d$−(C$_d$)(I)	92.63	—	38.49	41.42	41.84	43.10	43.10	42.26	—
C$_t$−(Cl)	—	139.75	33.05	35.15	36.40	37.66	39.33	40.17	—
C$_t$−(Br)	—	151.04	34.73	36.40	37.66	38.49	39.75	40.58	—
C$_t$−(I)	—	158.57	35.15	36.82	38.07	38.91	40.17	41.00	—
C$_b$−(F)	−179.08	67.36	26.36	31.80	35.56	38.07	41.00	42.68	—
C$_b$−(Cl)	−15.90	79.08	30.96	35.15	38.49	40.58	42.68	43.51	—

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
$C_b-(Br)$	44.77	90.37	32.64	36.40	39.33	41.42	43.10	43.93	—
$C_b-(I)$	100.42	99.16	33.47	37.24	40.17	41.42	43.10	43.93	—
$C-(C_b)(F)_3$	−680.74	179.08	52.3	64.02	71.96	77.40	84.10	87.86	—
$C-(C_b)(Br)(H)_2$	−28.87	—	38.87	46.44	52.17	57.28	65.23	69.91	—
$C-(C_b)(I)(H)_2$	35.15	—	40.92	48.37	53.97	58.91	66.44	70.75	—
$C-(Cl)_2(CO)(H)$	−74.48	—	53.56	61.71	66.85	69.66	75.02	77.66	—
$C-(Cl)_2(CO)$	−82.01	—	71.13	78.45	81.80	83.47	86.32	87.28	—
$CO-(Cl)(C)$	−126.36	—	37.11	39.50	42.84	46.36	52.43	56.86	—
Corrections for Groups Neighbouring with a Halogen									
ortho (F)(F)	20.92	—	0	0	0	0	0	0	0
ortho (Cl)(Cl)	9.20	—	−2.09	−1.84	−2.30	−2.22	−1.17	−0.08	—
ortho (alkane) (halogen)	2.51	—	1.76	1.84	1.17	0.79	0.50	0.59	—
cis (halogen) (halogen)	1.26	—	−0.79	−0.04	−0.13	−0.71	0	−0.13	—
cis (halogen) (alkane)	−3.35	—	−4.06	−2.93	−2.22	−1.97	−1.00	−0.54	—
Sulphur-Containing Groups									
$C-(H)_3(S)$	−42.17	127.23	25.90	32.80	39.33	45.14	54.47	61.80	
$C-(C)(H)_2(S)$	−23.64	41.34	22.51	29.62	35.98	41.71	51.29	59.20	
$C-(C)_2(H)(S)$	−11.04	−47.36	20.29	27.24	32.55	36.36	41.42	44.22	
$C-(C)_3(S)$	−2.30	−143.97	19.12	26.23	31.17	34.10	36.48	33.89	
$C-(C_b)(H)_2(S)$	−19.79		17.20	28.24	36.40	42.47	49.91	54.81	
$C-(C_d)(H)_2(S)$	−26.99		20.92	29.25	36.27	42.13	51.92	59.79	
$C_b-(S)$	−7.53	42.68	16.32	22.17	25.94	27.61	28.87	28.87	
$C_d-(H)(S)$	35.81	33.47	17.40	21.04	24.31	27.20	32.01	35.35	
$C_d-(C)(S)$	45.73	−51.92	14.64	14.94	16.02	17.11	18.45	20.92	
$S-(C)(H)$	19.33	136.94	24.52	25.94	27.24	28.37	30.54	32.26	
$S-(C_b)(H)$	50.04	52.97	21.42	22.01	23.30	25.23	29.25	32.80	
$S-(C)_2$	48.16	55.02	20.88	20.75	21.00	21.21	22.63	23.97	

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
S−(C)(C_d)	41.71		17.66	21.25	23.26	24.14	24.56	24.56	
S−(C_d)$_2$	−18.99	68.95	20.04	23.35	23.14	26.32	33.22	40.71	
S−(C_b)(C)	80.16		12.63	14.18	15.52	16.90	19.33	29.92	
S−(C_b)$_2$	108.36		8.37	8.41	9.37	11.46	15.90	19.71	
S−(S)(C)	29.50	51.76	21.88	22.68	23.05	23.05	22.51	21.42	
S−(S)(C_b)	60.67		12.79	14.18	15.56	17.36	20.00	21.34	
S−(S)$_2$	12.72	55.90	19.66	20.92	21.34	21.76	22.17	22.59	
C−(SO)(H)$_3$	−42.17	127.23	25.90	32.80	39.33	45.14	54.47	61.80	
C−(C)(SO)(H)$_2$	−32.30		19.04	26.86	33.26	38.32	45.81	51.13	
C−(C)$_3$(SO)	−12.76		12.80	19.16	20.25	27.61	31.55	33.30	
C−(Cd)(SO)(H)$_2$	−30.75		18.41	26.61	29.04	38.70	45.90	51.25	
C_b−(SO)	9.62		11.17	13.14	15.40	17.36	20.75	22.76	
SO−(C)$_2$	−60.29	75.73	37.15	41.96	43.93	45.14	45.94	46.73	
SO−(C_b)$_2$	−50.21		23.93	38.03	40.58	47.91	47.95	47.07	
C−(SO_2)(H)$_3$	−42.17	127.23	25.90	32.80	39.33	45.14	54.47	61.80	
C−(C)(SO_2)(H)$_2$	−32.13		22.51	29.62	35.98	41.71	51.30	59.20	
C−(C)$_2$(SO_2)(H)	−10.96		18.49	26.15	31.63	36.48	40.33	43.10	
C−(C)$_3$(SO_2)	−2.55		9.71	18.32	23.85	27.15	30.42	31.21	
C−(C_d)(SO_2)(H)$_2$	−29.87		20.92	29.25	36.27	42.13	51.92	59.79	
C−(C_b)(SO_2)(H)$_2$	−23.18		15.52	27.49	34.64	40.96	49.75	55.23	
C_b−(SO_2)	9.62		11.17	13.14	15.40	17.36	20.75	22.76	
C_d−(H)(SO_2)	52.42		12.72	19.54	24.81	28.62	32.93	36.27	
C_d−(C)(SO_2)	60.54		7.74	13.01	16.65	19.25	22.30	23.72	
SO_2−(C)$_2$	−291.79	87.44	42.59	42.12	54.06	57.61	63.30	66.94	
SO_2−(C)(C_b)	−302.46		41.59	48.12	56.27	60.71	65.35	66.61	
SO_2−(C_b)$_2$	−286.94		34.98	46.15	56.69	62.51	66.36	66.78	
SO_2−(C_d)(C_b)	−286.94		41.38	48.12	55.86	64.13	65.77	66.61	
SO_2−(C_d)$_2$	−307.86		48.20	50.08	55.86	59.75	64.35	66.44	
SO_2−(SO_2)(C_b)	−319.03		41.04	43.12	56.57	61.63	65.73	67.07	

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
CO–(S)(C)	−132.05	64.56	23.39	26.44	29.66	32.47	37.19	40.21	
S–(H)(CO)	−5.90	130.54	31.92	33.85	33.97	34.18	35.56	34.48	
C–S(F)$_3$	—	162.76	41.34	54.43	61.05	68.49	76.02	79.96	
S–(C)(CN)	155.56	171.79	39.79	43.68	46.94	49.62	53.76	56.48	
CS–(N)$_2$	−132.05	64.56	23.39	26.44	29.66	32.48	37.19	40.21	
N–(CS)(H)$_2$	53.47	122.13	25.40	30.46	34.22	37.28	42.22	45.94	
S–(S)(N)	−20.50		15.48	15.48	15.48	15.48	17.57	17.57	
N–(S)(C)$_2$	125.10		16.61	21.63	25.98	29.04	30.92	38.66	
SO–(N)$_2$	−132.05		23.38	26.44	29.66	32.47	37.19	40.21	
N–(SO)(C)$_2$	66.94		17.57	24.60	25.61	27.32	28.58	34.89	
SO$_2$–(N)$_2$	−132.05		23.38	26.44	29.66	32.47	37.19	40.21	
N–(SO$_2$)(C)$_2$	−85.35		25.19	26.57	31.55	34.43	37.78	38.45	
Correction for Cyclic Sulphur-Containing Groups (σ)									
(2)	74.06	123.30	−11.92	−10.84	−11.13	−12.63	−18.07	−24.35	
(2)	81.04	113.72	−19.20	−17.49	−16.36	−16.36	−19.25	−23.85	
(2)	7.24	98.57	−20.50	−19.54	−15.40	−15.31	−18.45	−23.30	
(2)	0	73.05	−26.02	−17.82	−9.37	−2.63	3.60	5.40	

Table A.6 (*continued*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
(2)	16.27		−32.43	−20.58	−5.10	10.84	20.04	19.29	
(2)	21.21		−26.94	−17.74	−17.70	−17.49	−20.08	−24.94	
(2)	21.21		−26.94	−17.74	−17.70	−17.49	−20.08	−24.94	
(2)	24.02		−20.50	−19.54	−15.40	−15.31	−18.45	−23.30	
(2)	7.24	98.57	−20.50	−19.54	−15.40	−15.31	−18.45	−23.30	

Table A.6 (*concluded*)

Groups	ΔH_f°, kJ/mol	S°, J/(mol·K)	C_p°, J/(mol·K) at T, K						
			300	400	500	600	800	1000	1500
Organo-Phosphorus Groups									
C–(P)(H)$_3$	−42.17	127.23	C–(P)(H)$_3$ ≡ C–(C)(H)$_3$						
C–(P)(C)(H)$_2$	−10.33								
C–(PO)(H)$_3$	−42.17		C–(PO)(H)$_3$ ≡ C–(C)(H)$_3$						
C–(PO)(C)(H)$_2$	−14.22								
C–(P:N)(H)$_3$	−42.17		C–(PN)(H)$_3$ ≡ C–(C)(H)$_3$						
C–(N:P)(C)(H)$_2$	81.17								
C$_b$–(P)	−7.53		C$_b$–(P) ≡ C$_b$–(O)						
C$_b$–(PO)	9.62		C$_b$–(P) ≡ C$_b$–(CO)						
C$_b$–(P:N)	9.62		C$_b$–(P : N) ≡ C$_b$–(CO)						
P–(C)$_3$	29.45								

* The values of the corrections for the entropy are 5 for butenes, 0 for 2-alkenes (β-olefins), and 2.5 for 1-alkenes (α-olefins).

** N_I is nitrogen with a double bond in imines; N_I–(C$_b$) is nitrogen in pyridine; and N_a is nitrogen with a double bond in azo-compounds. The steric correction for hydrocarbons is +3.35 kJ/mol for ΔH_f°; add −6.28 kJ/mol per group for the *ortho*- and *para*-positions in pyridine; the corrections for the groups C–(N_a)(H)$_3$, C–(N)(H)$_3$, and C–(C)(H)$_3$ are the same.

Table A.7. **Cases When Corrections Must Be Introduced**

Substance	Correction				Miscellaneous
	for molecule branching	for feature of structure			
		cis	*ortho*	ring or steric difficulties	
Alkanes	ΔH_f°	—	—	—	—
Alkenes	ΔH_f°	ΔH_f°, S°, C_p°	—	—	—
Aromatics	—	—	ΔH_f°, S°, C_p°	—	—
Cycloalkanes	ΔH_f°	ΔH_f°, S°, C_p°	—	—	—
Polycyclic aromatics	—	—	ΔH_f°, S°, C_p°	ΔH_f°, S°, C_p°	for conjugation, to ΔH_f°
Ethers	ΔH_f°	—	—	—	—
Aliphatic nitrogen-containing	ΔH_f°	—	—	—	—

2. The symmetry number σ is used when calculating the entropy. The correction $-R \ln \sigma$ is added to the additive quantity, so that

$$S_{300}^\circ \approx S_{298}^\circ = S_{298,\mathrm{add}}^\circ - R \ln \sigma$$

$$\sigma = \sigma_{\mathrm{ext}} \Pi \sigma_{\mathrm{int},i}$$

where $\sigma_{\mathrm{int},i}$ and σ_{ext} are the number of internal and external axes of symmetry: $\sigma_{\mathrm{int},i} = 3$ for methyl and 2 for BF_2.

For example, for acetone $CH_3—CO—CH_3$, we have $\sigma = 2\,(3 \times 3) = 18$. If σ_{int} is evaluated as 3×3, then $\sigma_{\mathrm{ext}} = 2$.

The values of σ_{int}, σ_{ext}, and σ for selected substances are given below:

Substance			
Methanol	3	1	3
Acetic acid	3	1	3
Acetone	3^2	2	18
Trimethylamine	3^3	3	81
Benzene	1	6×2	12
Cyclohexane	1	6	6
para-Cresol	3	2	6
Aniline	1	2	2
1,2,4-Trimethylbenzene	3^3	1	27

For greater detail on the determination of σ, see [3, 9].

3. For optically active molecules (n is the number of isomers), the correction for calculating the entropy has the form $-R \ln (\sigma/n)$, i.e.

$$S^\circ_{300} \approx S^\circ_{298} = S^\circ_{298,\mathrm{add}} - R \ln \frac{\sigma}{n}$$

4. Conformation corrections are added for each interaction except when they have already been included in a group.

Example 1. *Thermodynamic Functions of Acetone.* Acetone contains two C—(H_3)C groups and a CO—$(C)_2$ group. Using the data in Table A.6, we find

$$\Delta H^\circ_f = 2(-42.17) - 131.38 = -215.72 \text{ kJ/mol}$$

(the tabulated value is −217.65, see p. 479).

The value of σ for acetone is 18 (see p. 410), hence

$$S^\circ_{298} = 2(127.2) + 62.80 - R \ln 18 = 293.30 \text{ J/(mol·K)}$$

(295.43 is the tabulated value).

$$C^\circ_p = 2 \times 25.9 + 25.39 = 77.19 \text{ J/(mol·K)}$$

(the tabulated value is 75.19).

Example 2. *The Heat of Formation of Triethylamine* $(CH_3CH_2)_3N$. Triethylamine contains three groups C—(H_3)(C), three groups C—$(H)_2$(C)(N), and the group N—$(C)_3$.

$$\Delta H^\circ_f = 3(-42.17) + 3(-27.61) + 102.09 + (3 \times 3.35) = -97.24 \text{ kJ/mol}$$

(− 99.83 is the tabulated value; 3.35 is a correction).

Example 3. *The Entropy of 1,1-Dimethylhydrazine* $(CH_3)_2NNH_2$. This compound contains two groups C—$(H)_3$(N) and the groups N—$(C)_2$(N) and N—(N)$\times$ $\times$ $(H)_2$. Two optical isomers exist: $n = 2$. We have $\sigma_{\mathrm{int}} = 3 \times 3$, $\sigma/n = (3 \times 3)/2 = 4.5$, and $-R \ln (\sigma/n) = -R \ln 4.5 = -12.47$. Hence,

$$S^\circ_{298} = 2 \times 127.43 + (-57.74) + (121.88) - 12.47 = 306.53 \text{ J/mol·K)}$$

(the tabulated value is 306.68).

Example 4. *The Entropy of Methylisopropylketone.* This ketone has no optical isomers. We have for it $\sigma_{\mathrm{ext}} = 1$, $\sigma_{\mathrm{int}} = 3^3$, and $\sigma = 27$. The contributions of the constituents are as follows:

C—(C)$(H)_3$—two groups	$2 \times 127.2 =$	254.4
C—$(C)_2$(H)(CO)		−50.21
CO—$(C)_2$		62.80
C—(CO)(H_3)		127.24
$-R \ln 27$		−27.41
	$S^\circ_{298} =$	366.82 J/(mol·K)

(the tabulated value is 370.3).

A1.3. Calculation of C°_p, S°, ΔH°_f, and log $K^\circ_{p,f}$ for Hydrocarbons at Various Temperatures and Numbers of Carbon Atoms in a Molecule

The method considered above is based on the introduction of the magnitudes of the changes in the thermodynamic functions attending a changa in the structure of a molecule. This method has been fa-

voured because of its simplicity and the possibility of using it for a broad range of compounds. It would be still more alluring to obtain working equations in which the corrections would be included as constant coefficients. Such equations were repeatedly proposed in the literature. Equations are known, for example, for calculating the heat of formation (in J/mol) of hydrocarbons with a different number n of carbon atoms, namely, for gaseous alkanes ($n \geqslant 5$):

$$\Delta H^{\circ}_{f,298} = 4.18\,[-10\,408 - 4296n \pm (164.8 - 38.84n \pm 2.893n^2)^{1/2}]$$

and for liquid alkanes ($n \geqslant 5$):

$$\Delta H^{\circ}_{f,298} = 4.18\,[-10\,887 - 6106n \pm (165.4 - 38.98n \pm 2.903n^2)^{1/2}]$$

A different dependence of the heat of formation of gaseous hydrocarbons on n is given by Stull *et al.* [26]:

$$\Delta H^{\circ}_{f,298} = 4.18\,(A + Bn' + C) \qquad (A.1)$$

The coefficients A, B, and C are chosen from Table A.8.

Table A.8. **Coefficients A, B, and C of Eq. (A.1)**

Coefficients	Alkanes $CH_3(CH_2)_{n'}H$	1-Alkenes $CH_2{=}CH(CH_2)_{n'}H$	Alkylbenzenes $C_6H_5(CH_2)_{n'}H$	Alkylcyclopentenes $C_5H_9(CH_2)_{n'}H$	Alkylcyclohexanes $C_6H_{11}(CH_2)_{n'}H$
A	−15.334	9.740	16.404	−20.516	−31.246
B	−4.926	−4.926	−4.926	−4.926	−4.926
C					
$n'=0$	−2.55±0.37	2.76±0.37	3.42±0.38	2.05±0.40	1.82±0.41
$n'=1$	0.02±0.33	0.07±0.33	0.47±0.34	−0.06±0.37	−0.82±0.40
$n'=2$	0.37±0.30	0.39±0.33	0.57±0.33	−0.01±0.36	0.05±0.45
Possible maximum errors of calculations	±0.3	±0.5	±0.35	±0.4	±0.4

We must not fail to note that previously relations such as $\Phi = \Phi(T)$ or $\Phi = \Phi(n)$ were obtained for a thermodynamic function Φ, but never $\Phi = \Phi(T, n)$. Moreover, the chosen form of the relation $\Phi = \Phi(n)$ does not seem to be felicitous.

In this connection, we have obtained expressions of the thermodynamic functions for the arguments T and n. When deriving them, we

took into consideration that the relation $\Phi(n)$ must be "combined" with thermodynamically substantiated equations $\Phi(T)$. The structure of these equations is substantiated below.

In accordance with the method of corrections, the known equation for the heat capacity of a substance, i.e.

$$C_p^\circ = a_i + b_i T + c_i T^2$$

can be transformed into an expression whose right-hand side will contain no quantities with the subscript i. Indeed, with a view to the method of corrections, we have

$$a = \alpha_0 + \alpha n,\ b = \beta_0 + \beta n, \text{ and } c = \delta_0 + \delta n$$

Hence, for C_p°, we obtain

$$C_p^\circ = (\alpha_0 + \alpha n) + (\beta_0 + \beta n)\, T + (\delta_0 + \delta n)\, T^2 \qquad \text{(A.2)}$$

It can be seen from Sec. A1.4 that the coefficients α_0, α, β_0, β, δ_0, and δ will be the same only for hydrocarbons of one type, therefore, Eq. (A.2) can be used for hydrocarbons of one group, for example, n-alkanes or n-1-alkenes.

Similarly, by processing data on the entropy of hydrocarbons of one type at different temperatures, we can obtain an equation of S° as a function of T and n. But it must be had in view that part of the coefficients of this equation are determined from the coefficients of the equation of C_p° as a function of T and n. Since

$$S^\circ(T,n) = S^\circ_{T_1}(n) + \int_{T_1}^{T} \frac{C_p^\circ}{T}\, dT$$

we have

$$S^\circ(T,n) = S^\circ_{T_1}(n) + (\alpha_0 + \alpha n) \ln \frac{T}{T_1} + (\beta_0 + \beta n)(T - T_1) + \frac{\delta_0 + \delta n}{2}(T^2 - T_1^2)$$

The relation $S^\circ(T_1,n)$ can be written in the form

$$S^\circ(T_1,\ n) \equiv S^\circ_{T_1}(n) - (\alpha_0 + \alpha n) \ln T_1 - (\beta_0 + \beta n)\, T_1 - \frac{\delta_0 + \delta n}{2} T_1^2 = \gamma_0 + \gamma n$$

and we thus have

$$S^\circ(T,\ n) = (\gamma_0 + \gamma n) + (\alpha_0 + \alpha n) \ln T + (\beta_0 + \beta n)\, T + \frac{\delta_0 + \delta n}{2} T^2 \qquad \text{(A.3)}$$

Since the coefficients α and δ are the same as in Eq. (A.2) for the heat capacities, we must determine the coefficients γ_0 and γ. For this purpose, we have calculated the values of $S^\circ(T_1, n)$ for similar structures and then determined the coefficients γ_0 and γ by the method of least squares.

Similar reasoning yields the following structure of the equation for the heat of formation of hydrocarbons of a single type:

$$\Delta H_f^\circ(T, n) = (a_0' + a'n) + (b_0' + b'n)T + (c_0' + c'n)T^2 + (d_0 + d_1 n)T^3 \ldots \quad (A.4)$$

The quantity $\log K_{p,f}^\circ$ used in thermodynamic calculations depends on the temperature as follows:

$$\log K_{p,f}^\circ = m' + l'\frac{1}{T} + q' \ln T + p'T + r'T^2$$

where m', l', q', p', and r' are parameters.

Calculations have shown, however, that this relation can be simplified with an accuracy adequate for practical purposes and can be written in the form

$$\log K_{p,f}^\circ = m' + l'\frac{1}{T} + p'T + r'T^2$$

If we now represent each of the parameters as a function of the number n of carbon atoms, using a linear relation, we obtain:

$$\log K_{p,f}^\circ(T, n) = (m_0 + mn) + (l_0 + ln)\frac{1}{T} + (p_0 + pn)T + (r_0 + rn)T^2 \quad (A.5)$$

As will be shown below, relations (A.2)-(A.5) are sufficiently accurate. Their application will be demonstrated for various types of compounds. One must only have in view that the corrections do not depend on n for the hydrocarbons C_4, C_5, and higher. Therefore the relations given below hold only for values of n exceeding four for alkanes and alkenes, and so on.

Normal Alkanes

The equations (A.2)-(A.5) for calculating the thermodynamic functions as applied to n-alkanes with four or more carbon atoms in the state of an ideal gas at temperatures of 300 to 1500 K are as follows:

$$C_p^\circ(T, n) = (-2.1 + 4.8n) + (27.60 + 69.11n)10^{-3}T - (0.53 + 2.19n)10^{-5}T^2 \text{ J/(mol·K)}$$

$$S^\circ(T, n) = (156.9 - 7.23n) + (-2.1 + 4.8n)\ln T + (27.60 + 69.11n)10^{-3}T - \frac{0.53 + 2.19n}{2} \times 10^{-5}T^2 \text{ J/(mol·K)}$$

$$-\Delta H_f^\circ(T, n) = (19.55 + 17.87n) + (95.18 + 12.58n)10^{-3}T - (8.12 + 0.62n)10^{-5}T^2 + (2.53 + 0.015n)10^{-8}T^3 \text{ kJ/mol}$$

$$-\log K_{p,f}^\circ(T, n) = (-1.67 + 4.54n) + (3.14 + 0.77n)10^{-3}T - (0.196 + 0.008n)10^{-5}T^2 - (2.45 + 0.97n)\frac{10^3}{T}$$

Table A.9. **Tabulated (Calculated) Values of the Thermodynamic Functions for *n*-Butane and *n*-Decane**

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	$-\Delta H_f^\circ$, kJ/mol	$\log K_{p,f}^\circ$
		n-Butane		
300	97.90 (100.0)	310.8 (312.4)	126.3 (124.4)	2.87 (2.93)
700	186.4 (184.4)	428.9 (430.0)	149.3 (149.8)	−10.67 (−10.71)
1100	237.2 (239.1)	524.8 (525.7)	156.6 (157.3)	−14.84 (−14.78)
1500	266.2 (264.2)	603.0 (604.2)	155.3 (158.2)	−16.82 (−16.44)
		n-Decane		
300	235.7 (241.3)	546.1 (551.7)	249.9 (252.4)	−6.09 (−6.27)
700	444.4 (439.1)	829.8 (833.4)	295.9 (292.0)	−32.95 (−32.68)
1100	559.4 (565.1)	1056.9 (1060.3)	307.3 (303.7)	−41.25 (−41.25)
1500	624.3 (619.3)	1241.0 (1245.3)	300.2 (298.0)	−45.03 (−45.69)

Table A.9 compares the tabulated [4, 26] and calculated values (given in parentheses) of the thermodynamic functions for *n*-butane and *n*-decane. The coincidence is good in all cases.

Alkenes

We obtained equations of the form of (A.2)-(A.5) for normal 1-alkenes with four or more carbon atoms in the state of an ideal gas at temperatures of 300 to 1500 K:

$$C_p^\circ(T, n) = (-4.4 + 5.50n) + (-12.40 + 68.29n)\,10^{-3}T + (0.6 - 2.15n)\,10^{-5}T^2 \text{ J/mol}$$

$$S^\circ(T, n) = (174 - 11.31n) + (-4.41 + 5.50n)\ln T + (-12.4 + 68.29n)\,10^{-3}\,T + \frac{0.57 - 2.15n}{2} \times 10^{-5}T^2 \text{ J/(mol·K)}$$

$$-\Delta H_f^\circ(T, n) = (-99.56 + 18.08n) + (69.88 + 10.71n)\,10^{-3}\,T - (7.40 + 0.14n)\,10^{-5}T^2 + (2.72 - 0.21n)\,10^{-8}T^3 \text{ kJ/mol}$$

$$-\log K_{p,f}^\circ(T, n) = (-6.53 + 4.34n) + (3.91 - 0.95n)\,10^3/T + (0.56 + 1.01n)\,10^{-3}T - (0.107 + 0.020n)\,10^{-5}T^2$$

Table A.10 compares data of standard thermodynamic tables with the values of the thermodynamic functions (in parentheses) calculated by the above relations for *n*-1-butene and *n*-1-decene. A glance at the table reveals that the calculations are quite accurate.

Table A.10. **Tabulated (Calculated) Values of the Thermodynamic Functions for *n*-1-Butene and *n*-1-Decene**

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	$-\Delta H_f^\circ$, kJ/mol	log $K_{p,f}^\circ$
		n-1-Butene		
300	86.1 (88.6)	306.1 (304.3)	0.25 (0.07)	−12.49 (−12.40)
700	162.0 (160.9)	409.7 (407.5)	18.9 (19.1)	−13.29 (−13.27)
1100	205.2 (207.6)	492.6 (490.6)	25.8 (25.4)	−13.89 (−13.71)
1500	229.6 (228.7)	559.9 (558.6)	26.1 (26.2)	−14.16 (13.5)
		n-1-Decene		
300	224.9 (232.9)	541.9 (541.7)	124.4 (126.6)	−21.34 (−21.12)
700	420.2 (417.5)	811.1 (811.0)	166.0 (167.9)	−35.50 (−34.83)
1100	526.8 (535.3)	1025.5 (1026.1)	176.7 (177.7)	−40.18 (−39.73)
1500	587.0 (586.1)	1198.9 (1201.1)	171.1 (169.6)	−42.33 (−42.15)

Corrections for Calculating the Thermodynamic Functions of Alkenes with an Internal Double Bond and Side Chains from the Data on the Functions of Normal 1-Alkenes

It is obvious that for alkenes we cannot limit ourselves to the above data because in addition to the normal 1-alkenes there can exist a large number of isomers differing in the position of the double bond in the carbon chain, the structure of the carbon skeleton, and the spatial arrangement of the atoms. For example, four isomers can exist for butenes, six, for pentenes, 20, for hexenes, and 48, for heptenes.

In [72], it is recommended to use corrections for determining the thermodynamic functions of alkenes with a various structure. These corrections take into account the change in the functions when going over from an *n*-1-alkene to an alkene of the given structure. These corrections take into account the changes in the heat capacity C_p°, the entropy S°, the heat of formation ΔH_f°, and the standard Gibbs energy of formation of the gaseous alkene $\Delta G_f^\circ = -RT \ln K_{p,f}^\circ$ for the following changes in a molecule:

(1) a growth in the length of the 1-alkene carbon chain by a CH_2 group:

$$R{-}(CH_2)_2{-}CH{=}CH_2 \rightarrow R{-}(CH_2)_3{-}CH{=}CH_2$$

(2) a transition of a 1-alkene to a *cis*-2 alkene:

$$R{-}CH_2{-}CH_2{-}CH{=}CH_2 \rightarrow R{-}CH_2{-}CH{=}CH{-}CH_3$$

(3) a transition of a *cis*-2-alkene to a *cis*-3-alkene:

$$\underset{cis\text{-}2}{R{-}CH_2{-}CH{=}CH{-}CH_3} \rightarrow \underset{cis\text{-}3}{R{-}CH{=}CH{-}CH_2{-}CH_3}$$

(4) a transition of a 1-alkene to a *trans*-2-alkene:

$$R{-}(CH_2)_2{-}CH{=}CH_2 \rightarrow \underset{trans\text{-}2}{R{-}CH_2{-}CH{=}CH{-}CH_3}$$

(5) a transition of a *trans*-2 alkene to a *trans*-3 alkene:

$$\underset{trans\text{-}2}{R{-}CH_2{-}CH{=}CH{-}CH_3} \rightarrow \underset{trans\text{-}3}{R{-}CH{=}CH{-}CH_2{-}CH_3}$$

(6) a transition of a 1-alkene to a 2-methyl-1-alkene:

$$R{-}CH_2{-}CH_2{-}CH{=}CH_2 \rightarrow R{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

(7) a transition of a 1-alkene to a 3-methyl-1-alkene:

$$R{-}CH_2{-}CH_2{-}CH{=}CH_2 \rightarrow R{-}\overset{\overset{CH_3}{|}}{CH}{-}CH{=}CH_2$$

(8) a transition of a 1-alkene to a 3,3-dimethyl-1-alkene:

$$R{-}(CH_2)_3{-}CH{=}CH_2 \rightarrow R{-}C(CH_3)_2{-}CH{=}CH_2$$

The corrections corresponding to the above transitions have been determined by averaging the changes for 5-15 identical transitions carried out for alkenes with a different molecular mass. Using these corrections and the thermodynamic parameters of 1-butene, one can determine the heat capacity, entropy, heat of formation, and the change in the standard Gibbs energy of formation for an alkene with the given structure within a broad temperature interval (from 300 to 1000 K). We must stress that the characteristics of 1-butene and the corrections given in the following tables relate to the gaseous state at 0.101 MPa (1 atm).

Table A.11 presents the thermodynamic parameters of 1-butene for temperatures from 300 to 1000 K and the corrections to these values when the length of the carbon chain is increased by a CH_2 group. The table can be employed to find the thermodynamic parameters of any 1-alkenes.

The changes in the thermodynamic parameters when going over from 1-alkenes to *cis*-2-alkenes and *trans*-2-alkenes and from 2-alkenes to 3-alkenes (to *cis*-3- and *trans*-3-isomers) are given in Table A.12 for the same temperature intervals. Using this table, one can determine the thermodynamic parameters of various normal alkenes with an internal double bond. The changes in the thermodynamic parameters in the skeleton isomerization of a 1-alkene with

Table A.11. **Thermodynamic Parameters of 1-Butene and Their Change When the Number of Carbon Atoms in the *n*-Alkene Chain Increases by One**

Parameter	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
C_p°, J/(mol·K) for 1-butene	86.1	108.9	129.4	147.0	162.0	174.9	186.1	195.9
correction for CH_2 group	23.0	29.0	34.5	39.1	43.0	46.3	49.1	51.6
S°, J/(mol·K) for 1-butene	306.1	334.1	360.6	385.8	409.6	432.1	453.4	473.5
correction for CH_2 group	39.1	46.5	53.6	60.3	66.6	72.6	78.2	83.5
ΔH_f°, kJ/mol for 1-butene	−0.2	−6.2	−11.3	−15.5	−18.9	−21.5	−23.5	−24.9
correction for CH_2 group	−20.6	−22.0	−23.0	−23.9	−24.5	−24.9	−25.1	−25.2
ΔG_f°, kJ/mol for 1-butene	71.7	96.7	123.0	150.2	178.2	206.4	235.1	263.9
correction for CH_2 group	8.6	18.5	28.8	39.2	49.8	60.5	71.2	81.9

Table A.12. **Changes in the Thermodynamic Parameters of Alkenes in Their Structural and *cis-trans*-Isomerization**

Isomerization	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
				ΔC_p°, J/(mol·K)				
1 → *cis*-2	−7.1	−6.5	−5.3	−4.3	−3.7	−3.1	−2.5	−2.0
1 → *trans*-2	+0.3	−1.0	−1.5	−1.9	−1.8	−1.7	−1.7	−1.4
cis-2 → *cis*-3	−2.0	−0.4	0	+0.8	+0.4	+0.4	–	–
trans-2 → *trans*-3	+0.5	+2.1	+2.1	+2.1	+1.3	+1.3	+0.8	+0.8
				ΔS°, J/(mol·K)				
1 → *cis*-2	−0.9	−2.6	−4.2	−5.2	−5.7	−6.3	−6.4	−6.7
1 → *trans*-2	−6.2	−6.2	−6.7	−6.9	−7.2	−7.4	−7.8	−7.8
cis-2 → *cis*-3	−3.3	−7.5	−5.4	−7.1	−11.3	−6.7	−7.1	−7.1
trans-2 → *trans*-3	−5.9	−5.4	5.0	−5.4	−4.2	−4.2	−3.8	−3.8
				$\Delta(\Delta H_f^\circ)$, kJ/mol				
1 → *cis*-2	−6.9	−7.6	−8.1	−8.6	−9.0	−9.4	−9.6	−9.9
1 → *trans*-2	−10.9	−11.0	−11.1	−11.3	−11.5	−11.1	−11.8	−12.0
cis-2 → *cis*-3	0	0	0	0	0	0	0	0
trans-2 → *trans*-3	0	0	0	+0.4	+0.8	+0.8	+1.2	–
				$\Delta(\Delta G_f^\circ)$, kJ/mol				
1 → *cis*-2	−6.8	−7.1	−6.7	−6.3	−5.6	−4.8	−4.2	−3.2
1 → *trans*-2	−9.1	−8.8	−8.1	−7.5	−6.7	−5.8	−5.0	−4.2
cis-2 → *cis*-3	+2.1	+2.9	+3.3	+4.2	+5.0	+5.4	+6.7	+7.1
trans-2 → *trans*-3	+1.8	+2.5	+2.9	+3.3	+3.8	+4.2	+4.6	+4.6

Table A.13. **Change in the Thermodynamic Parameters with a Change in the Carbon Skeleton of an Alkene**

Parameter	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
	1-Alkene → 2-Methyl-1-alkene							
ΔC_p°, J/(mol·K)	+2.9	+2.7	+2.1	+1.5	+1.3	+1.0	+0.8	+0.7
ΔS°, J/(mol·K)	−6.2	−5.2	−4.9	−4.5	−4.1	−4.1	−4.0	−3.8
$\Delta(\Delta H_f^\circ)$, kJ/mol	−15.8	−15.5	−15.2	−15.1	−14.9	−14.8	−14.8	−14.8
$\Delta(\Delta G_f^\circ)$, kJ/mol	−14.1	−13.9	−13.5	−13.0	−12.7	−12.0	−11.4	−10.7
	1-Alkene → 3-Methyl-1-alkene							
ΔC_p°, J/(mol·K)	+10.9	+13.7	+14.4	+14.9	+15.6	+16.3	+16.8	+17.5
ΔS°, J/(mol·K)	−10.2	−6.6	−2.6	+0.7	+3.3	+5.6	+7.6	+9.7
$\Delta(\Delta H_f^\circ)$, kJ/mol	−6.2	−5.1	−3.6	−2.0	−0.3	+1.8	+2.7	+4.4
$\Delta(\Delta G_f^\circ)$, kJ/mol	−2.8	−2.9	−2.9	−3.2	−3.5	−3.9	−4.6	−5.2
	1-Alkene → 3,3-Dimethyl-1-alkene							
ΔC_p°, J/(mol·K)	−5.8	−4.7	−3.2	−2.1	−1.8	−1.8	−3.2	−2.3
ΔS°, J/(mol·K)	−41.0	−40.7	−40.1	−39.8	−39.4	−38.3	−38.2	−38.0
$\Delta(\Delta H_f^\circ)$, kJ/mol	−18.0	−18.6	−18.6	−19.0	−19.4	−19.3	−20.2	−20.5
$\Delta(\Delta G_f^\circ)$, kJ/mol	−5.8	−2.9	+0.9	+3.9	+7.7	+10.8	+13.8	+17.5

the appearance of one or two methyl groups in the side chain are given in Table A.13.

It is not difficult to calculate the thermodynamic parameters of alkenes of various structures using the data of Tables A.11-A.13. For example, if it is necessary to find the entropy of *cis*-2-methyl-2-butene in the gas state at 300 K, the calculations are based on the following transitions:

$$CH_3{-}CH_2{-}CH{=}CH_2 \rightarrow CH_3{-}(CH_2)_2{-}CH{=}CH_2 \rightarrow$$

$$\rightarrow CH_3{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 \rightarrow CH_3{-}CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3$$

In accordance with these transitions and the data of Tables A.11-A.13, the entropy of *cis*-2-methyl-2-butene is

$$S^\circ_{300} = 306.1 + 39.1 - 6.2 - 0.9 = 338.1 \text{ J/(mol·K)}$$

The true value is 339.8 J/(mol·K) [4, 26], i.e. differs from that calculated by the proposed method by about 0.5%.

In calculations with the aid of Tables A.11-A.13, the discrepancies do not exceed 0.6 J/(mol·K) (less than 0.3%) for the heat capacity, 0.4 kJ/mol (less than 0.8%) for the heat of formation, and 1.6 kJ/mol (less than 0.5%) for the change in the Gibbs energy. The good coincidence of tabulated data and the values calculated by the described method makes its use expedient for practical calculations.

Normal Alkylcyclopentane Hydrocarbons

Equations (A.2)-(A.5) for calculating the thermodynamic functions of *n*-alkylcyclopentane hydrocarbons with six and more carbon atoms in the state of an ideal gas at 300-1500 K acquire the following forms:

$$C^\circ_p(T, n') = (-19.49 + 3.75n') + (399.96 + 70.73n')\,10^{-3}T - (12.65 + 2.21n')\,10^{-5}T^2 \text{ J/(mol·K)}$$

$$S^\circ(T, n') = (299.82 - 2.04n') + (-19.49 + 3.75n')\ln T + (399.96 + 70.73n')\,10^{-3}T - \frac{12.65 + 2.21n'}{2}\,10^{-5}T^2 \text{ J/(mol·K)}$$

$$-\Delta H^\circ_f(T, n') = (47.35 + 14.30n') + (161.16 + 27.39n')\,10^{-3}T - (11.36 + 2.14n')\,10^{-5}T^2 + (2.46 + 0.49n')\,10^{-8}T^3 \text{ kJ/mol}$$

$$-\log K^\circ_{p,f}(T, n') = (-2.23 + 13.12n') + (32.51 - 10.59n')\,10^{-3}T + (-1.23 + 0.42n')\,10^{-5}T^2 - (0.22 + 2.75n')\,10^3/T$$

$$(n' = n - 5)$$

Table A.14 compares the tabulated values of the thermodynamic functions for *n*-propylcyclopentane and *n*-pentylcyclopentane with

Table A.14. **Tabulated (Calculated) Values of the Thermodynamic Functions for *n*-Propylcyclopentane and *n*-Pentylcyclopentane**

T, K	C_p°, J/(mol·K)	S°, (J/mol·K)	$-\Delta H_f^\circ$, kJ/mol	$\log K_{p,f}^\circ$
		n-Propylcyclopentane		
300	155.80 (158.02)	418.23 (421.71)	148.31 (148.31)	−9.368 (−9.07)
700	331.80 (325.79)	622.33 (621.01)	186.40 (186.82)	−25.783 (−25.65)
1100	426.77 (431.84)	794.42 (792.83)	194.97 (195.08)	−30.934 (−30.5)
1500	479.06 (476.19)	934.58 (934.88)	187.86 (187.83)	−33.423 (−33.17)
		n-Pentylcyclopentane		
300	201.80 (204.01)	496.43 (500.8)	189.2 (189.8)	−12.424 (−11.5)
700	417.77 (410.65)	755.67 (753.7)	234.93 (236.1)	−33.245 (−33.44)
1100	533.88 (541.46)	971.48 (970.07)	245.18 (245.2)	−39.740 (−38.72)
1500	598.31 (596.47)	1146.96 (1148.02)	235.98 (235.4)	−42.853 (−42.99)

the values calculated by the above formulas (given in parentheses). The coincidence is quite satisfactory. If it is necessary to determine the functions for an alkylcyclopentane with a branched side chain, it is convenient to use the corrections given in paragraph A.1.2 to the functions for the relevant *n*-alkylcyclopentane.

Normal Alkylcyclohexane Hydrocarbons

Equations (A.2)-(A.5) for calculating the thermodynamic functions of *n*-alkylcyclohexane hydrocarbons with seven and more carbon atoms in the state of an ideal gas at 300-1500 K acquire the following forms:

$$C_p^\circ(T, n'') = (-25.61 + 5.56n'') + (517.53 + 68.30n'')10^{-5}T^2 \text{ J/(mol·K)}$$

$$S^\circ(T, n'') = (305.45 - 12.42n'') + (-25.61 + 5.56n'') \ln T + (517.53 + 68.30n'')\, 10^{-3}T - \frac{16.90 + 2.15n''}{2} \times 10^{-5}T^2 \text{ J/(mol·K)}$$

$$-\Delta H_f^\circ(T, n'') = (87.04 + 14.78n'') + (206.7 + 18.7n'')\, 10^{-3}T - (16.78 + 1.26n'')\, 10^{-5}T^2 + (3.97 + 0.22n'')\, 10^{-8}T^3 \text{ kJ/mol}$$

$$-\log K_{p,f}^\circ(T, n'') = (5.89 + 8.18n'') + (27.38 - 1.03n'')\, 10^{-3}T + (-1.09 + 0.09n'')\, 10^{-5}T^2 - (2.57 + 2.02n'')\, 10^3/T$$

$$(n'' = n - 6)$$

Table A.15 compares the tabulated values of the thermodynamic functions for *n*-propylcyclohexane and *n*-pentylcyclohexane with the values calculated by the above formulas (given in parentheses). The coincidence of the calculated and tabulated values is good. If

Table A.15. **Tabulated (Calculated) Values of the Thermodynamic Functions for *n*-Propylcyclohexane and *n*-Pentylcyclohexane**

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	$-\Delta H_f^\circ$, kJ/mol	$\log K_{p,f}^\circ$
		n-Propylcyclohexane		
300	185.43 (187.3)	420.70 (423.5)	193.59 (193.0)	−8.493 (−8.24)
700	380.37 (382.9)	660.82 (660.5)	231.08 (230.3)	−29.461 (−31.13)
1100	495.80 (503.7)	861.49 (859.1)	233.89 (233.28)	−35.822 (−36.39)
1500	551.87 (549.9)	1024.24 (1023.8)	219.66 (218.9)	−38.726 (−42.67)
		n-Pentylcyclohexane		
300	231.42 (235.0)	498.90 (501.1)	234.18 (231.6)	−11.68 (−10.7)
700	476.56 (468.0)	794.21 (791.2)	279.28 (275.2)	−36.948 (−41.23)
1100	603.33 (612.5)	1038.47 (1036.2)	283.26 (279.2)	−44.667 (−52.12)
1500	671.11 (668.6)	1236.79 (1236.7)	307.36 (307.7)	−48.171 (−57.52)

it is necessary to determine the functions for an alkylcyclohexane with a branched side chain, the corrections given in paragraph A.1.2 can be added to the functions for the relevant *n*-alkylcyclohexane.

Normal Alkylbenzenes

Equations (A.2)-(A.5) for calculating the thermodynamic functions of *n*-alkylbenzenes with seven and more carbon atoms in the state of an ideal gas at 300-1500 K acquire the following forms:

$$C_p^\circ(T,\ n'') = (-4.39 + 5.17n'') + (321.43 + 69.05n'')\,10^{-3}\,T - (10.60 + 2.18n'')\,10^{-5}T^2 \text{ J/(mol·K)}$$

$$S^\circ(T,\ n'') = (216.32 - 9.15n'') + (-4.39 + 5.17n'')\ln T + (321.43 + 69.05n'')\,10^{-3}T - \frac{10.60 + 2.18n''}{2} \times 10^{-5}T^2 \text{ J/(mol·K)}$$

$$\Delta H_f^\circ(T,\ n'') = (-92.70 + 14.91n'') + (88.64 + 26.63n'')\,10^{-3}T - (5.69 + 2.16n'')\,10^{-5}T^2 + (1.23 + 0.53n'')\,10^{-8}T^3 \text{ kJ/mol}$$

$$-\log K_{p,f}^\circ(T,\ n'') = (6.54 + 4.70n'') + (2.96 + 0.83n'')\,10^{-3}T - (0.084 + 0.027n'')\,10^{-5}T^2 + (3.79 - 1.07n'')\,10^3/T$$

$$(n'' = n - 6)$$

Table A.16 compares the tabulated values of the thermodynamic functions for *n*-propylbenzene and *n*-pentylbenzene with the values calculated by the above formulas (given in parentheses). The coincidence of these values is good. To determine the thermodynamic

Table A.16. **Tabulated (Calculated) Values of the Thermodynamic Functions for *n*-Propylbenzene and *n*-Pentylbenzene**

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	$\log K_{p,f}^\circ$
		n-Propylbenzene		
300	152.34 (154.3)	401.66 (403.1)	7.61 (7.6)	−24.045 (−24.5)
700	303.88 (297.1)	593.17 (589.7)	−19.25 (−19.9)	−24.492 (−24.57)
1100	379.32 (385.2)	747.93 (744.35)	−27.2 (−27.68)	−25.073 (−25.26)
1500	420.36 (418.3)	872.41 (870.16)	−25.1 (−26.18)	−25.41 (−25.59)
		n-Pentylbenzene		
300	199.12 (202.1)	480.20 (483.3)	34.69 (34.6)	−26.824 (−26.78)
700	389.87 (382.8)	726.89 (725.4)	69.2 (69.49)	−31.769 (−31.72)
1100	486.77 (494.6)	925.42 (928.0)	78.66 (77.93)	−33.815 (−33.78)
1500	539.74 (537.7)	1085.16 (1086.5)	74.5 (74.46)	−34.778 (−34.71)

functions for an alkylbenzene hydrocarbon with a branched side chain, it is convenient to add the corrections given in paragraph A.1.2 to the functions for the relevant *n*-alkylbenzene.

Alkynes (Acetylene Hydrocarbons)

Equations of the form of (A.2)-(A.5) for calculating the thermodynamic functions of *n*-1-alkynes with four and more carbon atoms in the state of an ideal gas at 300-1500 K are as follows:

$$C_p^\circ(T, n) = (7.0 + 5.56n) + (-72.0 + 68.19n)\,10^{-3}T + (2.43 - 2.15n)\,10^{-5}T^2 \text{ J/(mol·K)}$$

$$S^\circ(T, n) = (112.5 - 12.24n) + (7.0 + 5.56n)\ln T + (-72.0 + 68.19n)\,10^{-3}T + \frac{2.43 - 2.15n}{2} \times 10^{-5}T^2 \text{ J/(mol·K)}$$

$$\Delta H_f^\circ(T, n) = (255.42 - 18.10n) - (30.16 + 10.48n)\,10^{-3}T + (4.41 + 0.12n)\,10^{-5}T^2 - (2.02 - 0.22n)\,10^{-8}T^3 \text{ kJ/mol}$$

$$-\log K_{p,f}^\circ(T, n) = (-11.76 + 4.20n) - (1.26 - 1.18n)\,10^{-3}T - (0.04 + 0.024n)\,10^{-5}T^2 + (12.44 - 0.92n)\,10^{-3}/T$$

Table A.17 compares the tabulated values of the thermodynamic functions for butyne (ethylacetylene) and decyne (octylacetylene) with the values calculated by the above formulas (given in parentheses). The coincidence of these values is satisfactory.

Table A.17. **Tabulated (Calculated) Values of the Thermodynamic Functions for Butyne and Decyne**

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	$\log K_{p,f}^\circ$
		Butyne (Ethylacetylene)		
300	81.46 (83.9)	291.2 (287.8)	165.1 (165.5)	−35.22 (−34.24)
700	140.46 (139.5)	384.5 (380.2)	152.8 (152.6)	−19.294 (−19.28)
1100	173.30 (175.4)	455.5 (451.3)	147.15 (147.5)	−15.225 (−15.08)
1500	192.38 (191.6)	512.3 (508.4)	145.85 (145.8)	−13.37 (−12.89)
		Decyne (Octylacetylene)		
300	220.71 (228.4)	525.8 (521.3)	41.05 (39.0)	−44.14 (−43.95)
700	398.74 (396.1)	784.1 (780.3)	5.8 (7.9)	−41.56 (−40.88)
1100	495.80 (502.7)	986.8 (983.1)	−3.6 (−4.4)	−41.508 (−41.39)
1500	550.61 (548.4)	1149.5 (1147.3)	1.0 (2.6)	−41.531 (−41.91)

A1.4. Thermodynamic Functions of Group Components Characterizing Complex Hydrocarbon Mixtures

Hundreds, and sometimes thousands, of individual substances participate in the conversions of petroleum fractions, and thousands of reactions proceed simultaneously. The thermodynamic and kinetic calculations of the conversions of petroleum fractions are possible only by combining structures of a single type into one group component. Next the possible conversions of the group components are considered. Such an approach is fruitful in kinetic analysis and in modelling production processes in petroleum refining and petroleum chemistry [8, 13]. It is also natural to employ this method for calculating the equilibrium compositions in conversions of petroleum fractions. In this case, the thermodynamic characteristics of the conversions of a mixture of hydrocarbons are calculated by using standard thermodynamic quantities for the individual hydrocarbons representing the initial and final mixtures. The individual hydrocarbons (they are sometimes called pseudocomponents) are chosen so that their molecular masses (or boiling points) coincide with the molecular masses (or mean boiling points) of the hydrocarbon mixtures. Since one does not usually succeed in selecting an individual hydrocarbon whose molecular mass equals the required one, the following approximating procedure can be used [13].

1. Determine the molecular mass M of the raw material.

2. Choose two individual hydrocarbons close in structure to the hydrocarbons of the mixture; the molecular mass M_1 of one of them should be slightly larger and the mass M_2 of the second one slightly smaller than M.

3. Using the additivity rule, find the fractions of the hydrocar-

bons forming a mixture with the molecular mass M:

$$M = M_1x_1 + M_2x_2 = \sum_i M_ix_i$$

4. Using the same rule and the found values, determine the thermodynamic quantities for the pseudocomponent substituting for the mixture:

$$\Delta H_f^\circ = \sum_i \Delta H_{f,i}^\circ x_i, \quad S^\circ = \sum_i S_i^\circ x_i, \quad C_p^\circ = \sum_i C_{p,i}^\circ x_i$$

5. Next calculate K_p° and the equilibrium composition for the pseudocomponents.

Equations (A.2)-(A.5) describing how the thermodynamic functions Φ depend on T and n reveal that the difference $\Delta\Phi = \Phi_i(T, n) - \Phi_j(T, n)$ (where i and j are subscripts designating different groups of hydrocarbons) depends only slightly on n. For example, if i stands for normal alkenes and j for normal alkanes, while Φ is the heat capacity, we have:

$$\Delta C_p^\circ(T, n) = (-2.3 + 0.7n) - (40.0 + 0.82n)\,10^{-3}T + (1.13 + 0.04n)\,10^{-5}T^2 \text{ J/K}$$

and

$$\left(\frac{\partial \Delta C_p^\circ}{\partial n}\right)_T = 0.7 - 0.82 \times 10^{-3}T + 0.04 \times 10^{-5}T^2$$

At 300 K, $(\partial\Delta C_p^\circ/\partial n)_T = 0.49$, and at 1000 K, $(\partial\Delta C_p^\circ/\partial n)_T = 0.28$. This signifies that when n grows by unity, ΔC_p° changes by 0.3-0.5 J/(mol·K), but this value is less than the error in determining ΔC_p° and it may be disregarded.

Similarly, the difference in the heats of formation (heats of the reactions) for the case when, for example, i stands for aromatics and j for normal alkanes is:

$$\Delta H^\circ = (-112.35 - 2.96n) + (-6.54 + 14.05n)\,10^{-3}T + (2.93 - 1.54n)\,10^{-5}T^2 + (-1.3 + 0.515n)\,10^{-8}T^3 \text{ kJ}$$

and

$$\left(\frac{\partial \Delta H^\circ}{\partial n}\right)_T = -2.96 + 14.05 \times 10^{-3}T - 1.54 \times 10^{-5}T^2 + 0.515 \times 10^{-8}T^3$$

At 300 K, $(\partial\Delta H^\circ/\partial n)_T = 0.1$ and at 1000 K, $(\partial\Delta H^\circ/\partial n) = 0.7$.

Consequently, the change in ΔH° when n grows by unity is within 0.1 to 0.7 kJ, which is also commensurable with the error in determining ΔH°.

Similar conclusions are reached when studying the change in the entropy, and also in the logarithm of the equilibrium constant of formation. Therefore, the values of ΔC_p°, ΔS°, ΔH°, and K_p for the reactions between the group components can be determined by calculating the thermodynamic functions of the group components by Eqs. (A.2)-(A.5) for the given temperature. The exact determination of the average number of carbon atoms is not so important if this number exceeds four for alkanes and alkenes and seven for alkylcycloalkanes or alkylbenzenes. It is also clear from this conclusion that group components with a fractional value of n may be replaced with individual substances for which the number of carbon atoms n_1 is close to n.

A1.5. Corrections for Determining the Standard Thermodynamic Functions of Hydrocarbon Derivatives from the Functions of the Hydrocarbons

Appendix 2 contains the standard thermodynamic functions of simple substances and compounds, including a large number of hydrocarbons. The thermodynamic functions of hydrocarbons can be used to find the relevant functions for their derivatives (oxygen-, nitrogen-, halogen-, and sulphur-containing ones) by introducing the corresponding corrections. The values of the corrections (Table A.18) given in this section have been found by Stull et al. [26] and by the author of this book by averaging the changes for specific compounds. When calculating the heat of formation and the entropy of a substance for elevated temperatures, one can use the approximate conditions: $\overline{C_p^\circ}$ for any temperature from 298 to T approximately equals $C^\circ_{p,\overline{T}}$, where $\overline{T} = 0.5(298 + T)$. Further,

$$\Delta H_f^\circ \approx \Delta H^\circ_{f,298} + \Delta C^\circ_{p,\overline{T}}(T - 298)$$

$$S^\circ \approx S^\circ_{298} + C^\circ_{p,\overline{T}} \ln (T/298)$$

Appendix 2

Tables of Standard Thermodynamic Functions for Simple Substances, Selected Inorganic Compounds, Hydrocarbons and Their Derivatives

The tables of the standard thermodynamic functions given in this Appendix have been compiled on the basis of data contained in [4, 35, 66] and chiefly in [26]. They are intended for the rapid performance of thermodynamic calculations of reactions of hydrocarbons and their derivatives. Unless otherwise indicated, the functions are given for the state of an ideal gas.

In the following tables, C_p° and S° are measured in J/(mol·K), ΔH_f° and ΔG_f°, in kJ/mol, and K_p° is dimensionless.

The thermodynamic functions for substances in the state of an ideal gas can be used to find similar functions for a real gas and a condensed state. The expressions for these calculations and examples of the calculations are given in Chapters 1 and 2 and in Appendix 1.

Table A.18. **Corrections for Determining the Standard Thermodynamic Functions of Hydrocarbon Derivatives in the State of an Ideal Gas from the Functions of the Hydrocarbons**

Corrections	Oxygen-containing derivatives		
	n-R-CH_2-R′-n → n-R-O-R′-n	n-R-CH_3 → n-R-OH	n-R-CH_2-CH_3 → n-R-CH=O
$\Delta(\Delta H^\circ_{f,298})$, kJ/mol	−105.0	−129.3	−59.7
ΔS°_{298}, J/(mol·K)	−5.19	−2.43	−19.60
ΔC°_p, J/(mol·K):			
300 K	−7.70	−10.09	−17.91
500 K	−19.81	−19.81	−34.76
700 K	−26.52	−26.81	−47.40
1000 K	−33.11	−34.18	−61.28

Corrections	Nitrogen-containing derivatives					
	R-CH_3 → R-NH_2	R-CH_2-R′ → R-NH-R′	R′, R″ R-C-H → R′, R″ R-N	R-CH_3 → R-CN	R-CH_3 → R-NO_2	R-CH_3 → R-ONO_2
$\Delta(\Delta H^\circ_{f,298})$, kJ/mol	59.90	79.50	100.42	161.08	2.18	−45.19
ΔS°_{298}, J/(mol·K)	−0.84	−2.51	−5.86	0.42	36.40	66.11
ΔC°_p, J/(mol·K):						
300 K	−1.75	−4.52	−5.06	−0.50	4.69	23.85
500 K	−7.32	−8.74	−8.33	−9.58	3.77	26.32
700 K	−11.94	−11.63	−10.71	−16.90	0.75	23.72
1000 K	−16.78	−15.23	−14.31	−25.10	−4.85	20.33

Table A.18 (*concluded*)

Corrections	Halogen-containing derivatives								
	R → CH_3 → R – F	R – $CH(CH_3)_2$ → R – CHF_2	Ar – CH_3 → Ar – F	R – CH_3 → R – Cl	Ar – CH_3 → Ar – Cl	R – CH_3 → R – Br	Ar – CH_3 → Ar – Br	R – CH_3 → R – I	Ar – CH_3 → Ar – I
$\Delta(\Delta H^\circ_{f,298})$, kJ/mol	−153.97	−342.67	−160.54	−6.99	1.84	38.49	55.02	95.40	—
ΔS°_{298}, J/(mol·K)	−20.79	−40.63	−27.03	−8.08	−14.14	2.51	−4.48	11.09	5.19
ΔC°_p, J/(mol·K):									
300 K	−14.94	−30.00	−10.04	−10.33	−5.76	−8.20	−6.11	−6.53	−3.05
500 K	−26.57	−53.30	−18.49	−22.51	−16.95	−20.04	−17.74	−19.00	−15.40
700 K	−35.40	−71.38	−28.07	−32.89	−28.07	−30.67	−28.57	30.00	−27.15
1000 K	−45.48	−91.42	−39.33	−44.02	−40.63	−42.63	−40.96	−42.13	−40.12

Corrections	Sulphur-containing derivatives		
	R – CH_3 → R – SH	R – CH_2 – R′ → R – S – R′	R – CH_2 – R′ → R – S – S – R′
$\Delta(\Delta H^\circ_{f,298})$, kJ/mol	58.28	64.89	71.80
ΔS°_{298}, J/(mol·K)	17.8	19.0	65.6
ΔC°_p, J/mol·K):			
300 K	−1.0	−3.5	21.0
500 K	−9.0	−12.0	14.5
700 K	−17.5	−17.5	7.0
1000 K	−27.5	−20.0	−2.5

Table A.19. **Thermodynamic Functions of Simple Substances**

T, K	Graphite C, solid		Hydrogen H_2, id. gas		Bromine Br_2, liquid		Chlorine Cl_2, id. gas		Fluorine F_2, id. gas	
	C_p°	S°	C_p°	S°	C_p°	S°	C_p°	S°	C_p°	S°
300	8.72	5.75	28.85	130.76	75.63	152.70	33.97	223.17	31.37	202.89
400	11.93	8.71	29.18	139.12	36.71	256.07	35.30	233.15	30.05	121.16
500	14.63	11.66	29.26	145.64	37.06	264.31	36.08	241.11	34.34	219.68
600	16.86	14.54	29.32	150.98	37.27	271.84	36.57	247.74	35.27	226.03
700	18.54	17.27	29.43	155.51	37.42	276.84	36.91	253.40	35.94	231.52
800	19.87	19.83	29.61	159.44	37.53	281.85	37.14	258.35	36.45	236.35
900	20.84	22.23	29.87	162.95	37.62	286.27	37.33	262.74	36.85	240.67
1000	21.50	24.46	30.20	166.12	37.70	290.24	37.47	266.67	37.17	244.57

T, K	Iodine I_2, solid		Nitrogen N_2, id. gas		Oxygen O_2, id. gas		Sulphur S_{rhomb}, solid	
	C_p°	S°	C_p°	S°	C_p°	S°	C_p°	S°
300	54.51	116.48	29.12	191.66	29.37	205.22	22.64	32.07
400	80.67	174.06	29.25	200.07	30.10	213.77	32.36	44.66
500	37.44	279.81	29.58	206.63	31.08	220.59	37.99	53.42
600	37.57	286.65	30.11	212.07	32.09	226.35	34.31	59.97
700	37.68	292.45	30.76	216.75	32.99	231.36	32.63	65.27
800	37.76	297.49	31.43	220.90	33.74	235.83	18.28	131.22
900	37.84	301.94	32.09	224.65	34.36	239.83	18.39	133.38
1000	37.91	305.93	32.70	228.06	34.87	243.48	18.48	135.33

Table A.20. **Thermodynamic Functions of Selected Inorganic Compounds**

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Ozone O_3			
300	39.29	238.95	142.26	162.92	−28.364
400	43.64	250.87	141.96	169.87	−22.181
500	47.11	261.00	141.92	176.86	−18.475
600	49.66	269.83	142.00	183.84	−16.004
700	51.46	277.65	142.17	190.79	−14.235
800	52.80	284.59	142.38	197.73	−12.909
900	53.81	290.87	142.63	204.64	−11.875
1000	54.56	296.60	142.84	211.50	−11.047
		Water H_2O			
300	33.60	188.95	−241.83	−228.53	39.788
400	34.27	198.70	−242.84	−223.93	29.241
500	35.23	206.48	−243.84	−219.07	22.887
600	36.32	212.96	−244.76	−214.05	18.634
700	37.45	218.65	−245.64	−208.86	15.585
800	38.70	223.76	−246.48	−203.55	13.290
900	39.96	228.36	−247.19	−198.15	11.499
1000	41.21	232.67	−247.86	−192.63	10.062
		Hydrogen Peroxide H_2O_2			
300	43.22	233.17	−136.15	−105.27	18.331
400	48.45	246.35	−137.40	−94.81	12.378
500	52.55	257.61	−138.32	−84.01	8.777
600	55.69	267.48	−138.99	−73.09	6.363
700	57.99	276.27	−139.53	−62.09	4.632
800	59.83	284.13	−139.91	−50.96	3.328
900	61.46	291.24	−140.25	−39.83	2.312
1000	62.84	297.80	−140.45	−28.66	1.497
		Hydrogen Sulphide H_2S			
300	34.22	206.02	−20.21	−33.14	5.771
400	35.60	216.02	−24.22	−37.11	4.845
500	37.24	224.13	−27.40	−39.96	4.174
600	38.99	231.08	−30.12	−42.22	3.673
700	40.79	231.23	−32.43	−43.93	3.278
800	42.59	242.80	−89.03	−50.75	3.313
900	44.31	247.90	−89.50	−45.90	2.665
1000	45.90	252.67	−89.83	−41.04	2.144
		Sulphur Dioxide SO_2			
300	39.96	248.36	−296.90	−300.20	52.267
400	43.47	260.37	−300.28	−301.04	39.309
500	46.57	270.41	−302.75	−300.95	31.437
600	49.04	279.11	−304.72	−300.37	26.149
700	50.96	286.85	−306.31	−299.45	22.343
800	52.42	293.76	−362.33	−303.67	19.826
900	53.60	299.99	−362.25	−296.31	17.198
1000	54.47	305.68	−362.17	−288.99	15.095

Table A.20 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Sulphur Trioxide SO_3			
300	50.75	256.35	−395.30	−370.24	64.458
400	58.83	272.08	−398.86	−361.54	47.212
500	65.52	285.98	−401.12	−351.96	36.767
600	70.71	298.40	−402.62	−341.96	29.769
700	74.73	309.62	−403.59	−331.66	24.749
800	77.86	319.78	−458.82	−326.64	21.328
900	80.46	329.11	−457.85	−310.20	18.003
1000	82.67	337.69	−456.72	−293.84	15.348
		Carbon Sulphide CS_2			
300	45.60	238.07	117.07	66.61	−11.596
400	49.45	251.75	111.59	50.08	−6.542
500	52.22	263.09	107.49	35.23	−3.678
600	54.27	272.80	104.06	21.09	−1.835
700	55.86	281.29	101.13	7.70	−0.574
800	57.07	288.82	−10.84	−16.07	1.050
900	57.99	295.60	−10.79	−16.74	0.971
1000	58.70	301.75	−10.75	−17.40	0.909
		Thionyl Chloride $SOCl_2$			
300	66.57	306.81	−211.71	−196.40	34.196
400	71.25	326.64	−214.39	−191.17	24.960
500	74.27	342.88	−216.10	−185.14	19.340
600	76.36	356.64	−217.36	−178.82	15.566
700	77.82	368.53	−218.32	−172.21	12.850
800	78.87	378.99	−273.68	−170.87	11.157
900	79.66	388.32	−272.84	−158.07	9.173
1000	80.25	396.73	−272.34	−145.31	7.591
		Sulphuryl Chloride SO_2Cl_2			
300	76.90	311.67	−357.31	−312.67	54.441
400	83.93	334.80	−360.33	−297.61	38.859
500	88.28	354.05	−362.25	−281.67	29.425
600	91.17	370.41	−363.63	−265.43	23.106
700	93.09	384.59	−364.72	−248.86	18.571
800	94.47	397.14	−420.20	−237.57	15.511
900	95.48	408.32	−419.65	−214.76	12.465
1000	96.23	418.40	−419.11	−192.04	10.031
		Sulphuric Acid H_2SO_4			
300	139.33	157.74	−813.54	−688.85	119.936
400	153.55	199.91	−812.28	−647.68	84.511
500	161.92	235.14	−809.44	−606.89	63.397
600	167.36	265.14	−805.80	−566.68	49.332
700	171.96	290.03	−801.65	−527.10	39.329

Table A.20 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Hydrogen Fluoride HF			
300	29.12	173.89	−271.12	−273.21	47.572
400	29.16	182.25	−271.29	−273.93	35.768
500	29.16	188.78	−271.50	−274.55	28.681
600	29.25	194.09	−271.79	−275.14	23.951
700	29.37	198.61	−272.13	−275.68	20.569
800	29.54	202.55	−272.46	−276.14	18.030
900	29.83	206.02	−272.80	−276.60	16.052
1000	30.17	209.20	−273.17	−277.02	14.470
		Hydrogen Chloride HCl			
300	29.12	186.98	−92.30	−95.31	16.592
400	29.16	195.35	−92.59	−96.27	12.570
500	29.29	201.88	−92.88	−97.15	10.148
600	29.58	207.23	−93.26	−97.95	8.528
700	30.00	211.84	−93.55	−98.70	7.366
800	30.50	215.85	−93.89	−99.45	6.492
900	31.04	219.49	−94.14	−100.12	5.810
1000	31.63	222.80	−94.39	−100.75	5.263
		Hydrogen Bromide HBr			
300	29.16	198.70	−36.27	−53.35	9.289
400	29.20	207.07	−52.05	−55.81	7.290
500	29.41	213.59	−52.42	−56.73	5.926
600	29.79	218.99	−52.80	−57.57	5.011
700	30.29	223.63	−53.14	−58.32	4.352
800	30.88	227.69	−53.43	−59.04	3.855
900	31.50	231.37	−53.68	−59.75	3.467
1000	32.13	234.72	−53.89	−60.38	3.154
		Hydrogen Iodide HI			
300	29.16	206.67	26.32	1.42	−0.248
400	29.33	215.10	16.99	−6.40	0.836
500	29.75	221.67	−5.65	−10.08	1.054
600	30.33	227.15	−5.98	−10.96	0.954
700	31.04	231.88	−6.23	−11.76	0.878
800	31.80	236.06	−6.48	−12.55	0.818
900	32.51	239.87	−6.61	−13.26	0.771
1000	33.14	243.30	−6.74	−14.02	0.732
		Carbon Monoxide CO			
300	29.16	198.11	−110.54	−137.44	23.931
400	29.33	206.52	−110.12	−146.48	19.128
500	29.79	213.09	−110.04	−155.60	16.254
600	30.46	218.57	−110.16	−164.68	14.337
700	31.17	223.34	−110.50	−173.76	12.966
800	31.88	227.57	−110.96	−182.76	11.933
900	32.59	231.33	−111.46	−191.71	11.126
1000	33.18	234.81	−112.00	−200.62	10.478

Table A.20 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Carbon Dioxide CO_2			
300	37.19	213.93	−393.50	−394.38	68.666
400	41.30	225.47	−393.59	−394.68	51.535
500	44.60	234.81	−393.67	−394.93	41.255
600	47.32	243.17	−393.80	−395.18	34.400
700	49.54	250.62	−394.01	−395.39	29.503
800	51.42	257.36	−394.22	−395.55	25.826
900	52.97	263.51	−394.42	−395.72	22.966
1000	54.27	269.16	−394.63	−395.85	29.676
		Nitrogen Monoxide NO			
300	29.83	210.87	90.37	86.65	−15.087
400	29.96	219.45	90.42	85.40	−11.153
500	30.50	226.19	90.46	84.14	−8.791
600	31.25	231.83	90.46	82.88	−7.217
700	32.05	236.69	90.46	81.63	−6.091
800	32.76	241.04	90.50	80.37	−5.247
900	33.43	244.93	90.50	79.12	−4.591
1000	33.97	248.49	90.54	77.82	−4.066
		Nitrogen Dioxide NO_2			
300	37.11	240.20	33.85	52.09	−9.070
400	40.33	251.33	33.26	58.28	−7.611
500	43.43	260.66	32.93	64.56	−6.746
600	46.11	268.82	32.76	70.92	−6.174
700	48.37	276.10	32.72	77.28	−5.766
800	50.21	282.67	32.76	82.64	−5.461
900	51.67	288.70	32.84	90.00	−5.223
1000	52.84	294.22	33.01	96.36	−5.032
		Ammonia NH_3			
300	35.69	192.84	−45.73	−15.98	2.783
400	38.66	203.51	−47.82	−5.73	0.749
500	42.01	212.50	−49.66	5.02	−0.522
600	45.23	220.41	−51.17	16.07	−1.400
700	48.28	227.65	−52.42	27.40	−2.044
800	51.17	234.26	−53.43	38.87	−2.537
900	53.85	240.45	−54.22	50.46	−2.928
1000	56.36	246.27	−54.85	62.13	−3.245
		Hydrazine N_2H_4			
300	52.76	240.54	95.10	158.91	−27.669
400	63.18	257.23	92.22	180.66	−23.590
500	70.71	272.17	90.12	203.01	−21.208
600	76.57	285.60	88.66	225.73	−19.652
700	81.59	297.77	87.65	248.65	−18.555
800	86.19	308.99	87.03	271.71	−17.740
900	89.96	319.36	86.73	294.85	−17.111
1000	93.30	328.99	86.65	317.98	−16.609

Table A.20 (*concluded*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Hydrogen Cyanide HCN			
300	36.02	201.96	130.54	120.04	−20.901
400	39.41	212.80	130.37	116.57	−15.223
500	42.01	221.88	130.16	113.13	−11.820
600	44.18	229.74	129.95	109.75	−9.555
700	46.15	236.69	129.70	106.40	−7.941
800	47.91	242.96	129.45	103.09	−6.732
900	49.50	248.70	129.20	99.83	−5.793
1000	50.96	254.01	128.99	96.57	−5.044
		Nitric Acid HNO_3			
300	53.85	266.77	−134.01	−73.34	12.767
400	63.64	283.67	−135.48	−52.84	6.900
500	71.50	298.74	−136.23	−32.09	3.352
600	77.70	312.33	−136.44	−11.21	0.977
700	82.47	324.68	−136.31	9.62	−0.718
800	86.36	335.97	−135.90	30.46	−1.989
900	89.41	346.31	−135.31	51.21	−2.973
1000	91.89	355.89	−134.56	71.92	−3.756

Table A.21. **Thermodynamic Functions of Individual Hydrocarbons**

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Alkanes			
		Methane CH_4			
300	35.77	186.52	−74.89	−50.67	8.823
400	40.63	197.44	−77.95	−42.13	5.502
500	46.53	207.15	−80.75	−32.84	3.432
600	52.51	216.15	−83.26	−23.05	2.005
700	58.20	224.68	−85.35	−12.80	0.957
800	63.51	232.80	−87.11	−2.34	0.154
900	68.37	240.58	−88.49	8.33	−0.484
1000	72.80	248.03	−89.54	19.16	−1.001
		Ethane C_2H_6			
300	52.89	229.83	−84.77	−32.59	5.675
400	65.61	246.81	−89.62	−14.43	1.886
500	78.07	262.80	−93.89	4.85	−0.508
600	89.33	278.07	−97.45	24.94	−2.171
700	99.24	292.59	−100.37	45.61	−3.402
800	108.07	306.44	−102.68	66.57	−4.347
900	115.85	319.62	−104.47	87.86	−5.100
1000	122.72	332.17	−105.77	109.33	−5.711

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Propane C_3H_8			
300	73.89	312.21	−103.97	−23.01	4.004
400	94.31	294.47	−110.29	4.98	−0.651
500	113.05	317.57	−115.56	34.43	−3.596
600	129.20	339.66	−119.91	64.85	−5.644
700	143.09	360.66	−123.34	95.94	−7.157
800	155.14	380.53	−125.98	127.40	−8.318
900	165.73	399.45	−127.95	159.20	−9.240
1000	175.02	379.74	−129.24	191.25	−9.988
		Butane C_4H_{10}			
300	97.91	310.75	−126.31	−16.48	2.869
400	123.85	342.50	−133.85	21.34	−2.784
500	147.86	372.79	−140.21	60.88	−6.358
600	168.62	401.62	−145.31	101.55	−8.841
700	186.40	428.99	−149.29	143.05	−10.674
800	201.79	454.88	−152.34	184.97	−12.078
900	215.22	479.44	−154.52	227.32	−13.193
1000	226.86	502.75	−155.85	269.87	−14.095
		Isobutane C_4H_{10}			
300	97.28	295.26	−134.68	−20.21	3.518
400	124.56	327.06	−142.21	19.16	−2.500
500	149.03	357.52	−148.45	60.21	−6.291
600	169.95	386.60	−153.43	102.42	−8.917
700	187.65	414.17	−157.32	145.39	−10.850
800	202.88	440.24	−160.25	188.82	−12.329
900	216.10	464.93	−162.30	232.63	−13.500
1000	227.61	488.31	−163.55	276.60	−14.448
		Pentane C_5H_{12}			
300	120.79	349.70	−146.61	−7.53	1.313
400	152.84	388.90	−155.52	40.21	−5.253
500	182.34	426.27	−162.92	90.04	−9.406
600	207.69	461.79	−168.87	141.21	−12.291
700	229.41	495.47	−173.47	193.26	−14.422
800	248.11	527.35	−176.90	245.85	−16.053
900	264.35	557.56	−179.28	298.90	−17.347
1000	278.45	586.14	−180.75	352.17	−18.394
		Isopentane C_5H_{12}			
300	119.41	344.34	−154.68	−13.97	2.431
400	152.67	383.34	−163.64	34.35	−4.486
500	182.88	420.74	−171.00	84.73	−8.851
600	208.74	456.39	−176.86	136.44	−11.876
700	230.91	490.28	−181.33	189.03	−14.105
800	249.83	522.37	−184.64	242.13	−15.809
900	266.35	552.79	−186.82	295.64	−17.159
1000	280.83	581.62	−188.03	349.36	−18.249

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Neopentane (2,2-Dimethylpropane) C_5H_{12}			
300	122.21	307.19	−166.15	−14.31	2.492
400	157.11	347.19	−174.77	37.66	−4.919
500	188.28	385.68	−181.63	91.59	−9.569
600	214.26	422.37	−186.94	146.73	−12.775
700	235.98	457.10	−190.87	202.71	−15.127
800	254.30	489.82	−193.72	259.12	−16.917
900	270.08	520.70	−195.52	315.85	−18.331
1000	283.68	549.90	−196.40	372.79	−19.471
		Hexane C_6H_{14}			
300	143.80	389.32	−167.40	0.75	−0.131
400	181.88	435.97	−177.61	58.41	−7.629
500	216.86	480.41	−186.10	118.45	−12.373
600	246.81	522.67	−192.88	179.99	−15.669
700	272.38	562.66	−198.07	242.59	−18.101
800	294.39	600.49	−201.92	305.77	−19.963
900	313.51	636.30	−204.56	369.45	−21.440
1000	330.08	670.23	−206.06	433.34	−22.635
		2-Methylpentane C_6H_{14}			
300	144.89	381.46	−174.51	−4.02	0.696
400	184.10	428.61	−184.56	54.43	−7.108
500	219.66	473.59	−192.80	115.19	−12.031
600	249.37	516.31	−199.30	177.36	−15.440
700	274.89	556.76	−204.22	240.58	−17.951
800	296.23	594.88	−207.86	304.34	−19.870
900	315.06	630.86	−210.33	368.57	−21.389
1000	331.32	664.92	−211.71	433.00	−22.616
		3-Methylpentane C_6H_{14}			
300	143.80	380.70	−171.84	−1.09	0.191
400	181.88	427.35	−182.05	57.45	−7.500
500	216.86	471.79	−190.54	118.32	−12.360
600	246.86	514.05	−197.32	180.71	−15.733
700	272.38	554.05	−202.51	244.18	−18.221
800	294.55	591.91	−206.35	308.24	−20.124
900	313.38	627.73	−208.99	372.75	−21.633
1000	330.12	661.62	−210.46	437.52	−22.853
		2,2-Dimethylbutane C_6H_{14}			
300	142.63	359.15	−185.77	−8.58	1.491
400	182.84	405.76	−196.02	52.13	−6.807
500	219.66	450.62	−204.30	115.14	−12.030
600	251.04	493.50	−210.71	179.66	−15.639
700	276.56	534.17	−215.48	245.14	−18.291
800	298.74	572.62	−218.91	311.12	−20.313
900	316.31	608.81	−221.20	377.56	−21.912
1000	333.46	643.04	−222.38	444.22	−23.202

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		2,3-Dimethylbutane C_6H_{14}			
300	141.25	366.64	−177.99	−3.05	0.529
400	181.16	412.84	−188.36	56.90	−7.433
500	217.15	457.23	−196.86	119.24	−12.458
600	247.69	499.61	−203.59	183.13	−15.941
700	273.63	539.78	−208.66	248.03	−18.506
800	295.81	577.81	−212.38	313.47	−20.466
900	314.64	613.75	−214.89	379.41	−22.018
1000	330.95	647.77	−216.27	445.55	−23.273
		Heptane C_7H_{16}			
300	166.77	428.94	−188.03	9.20	−1.602
400	210.96	483.08	−199.58	76.78	−10.025
500	251.33	534.59	−209.12	146.98	−15.355
600	285.89	583.54	−216.73	218.91	−19.058
700	315.39	629.90	−222.51	292.04	−21.792
800	340.70	673.67	−226.77	365.81	−23.883
900	362.67	715.13	−229.62	440.11	−25.541
1000	381.58	754.33	−231.21	514.67	−26.882
		2-Methylhexane C_7H_{16}			
300	166.77	421.04	−195.18	4.44	−0.770
400	210.96	475.18	−206.73	72.76	−9.503
500	251.33	526.68	−216.27	143.80	−15.021
600	285.89	575.63	−223.89	216.52	−18.848
700	315.39	621.99	−229.66	290.41	−21.671
800	340.70	665.76	−233.93	365.26	−23.829
900	362.67	707.22	−236.77	440.07	−25.539
1000	381.58	746.43	−238.36	515.43	−26.921
		3-Methylhexane C_7H_{16}			
300	166.77	425.18	−192.54	5.82	−1.012
400	210.96	493.32	−204.10	73.76	−9.631
500	251.33	530.82	−213.64	144.35	−15.080
600	285.89	579.78	−221.25	216.65	−18.861
700	315.39	626.14	−227.02	290.16	−12.651
800	340.70	669.90	−231.29	364.30	−23.785
900	362.67	711.36	−234.14	438.99	−25.476
1000	381.58	750.57	−235.73	513.92	−26.842
		3-Ethylpentane C_7H_{16}			
300	166.77	412.54	−189.91	12.26	−2.131
400	210.96	466.68	−201.46	81.46	−10.636
500	251.33	518.19	−211.00	153.30	−16.015
600	285.89	567.14	−218.61	226.90	−19.751
700	315.39	613.50	−224.39	301.62	−22.508
800	340.70	657.26	−228.66	377.02	−24.617
900	362.67	698.73	−231.50	452.96	−26.289
1000	381.58	737.93	−233.09	529.19	−27.640

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		2,2-Dimethylpentane C_7H_{16}			
300	166.77	393.92	−206.40	1.34	−0.233
400	210.96	448.06	−217.94	72.43	−9.455
500	251.33	499.57	−227.48	146.15	−15.266
600	285.89	548.52	−235.10	221.58	−19.288
700	315.39	594.88	−240.87	298.19	−22.250
800	340.70	638.65	−245.14	375.43	−24.513
900	362.67	680.11	−247.99	453.25	−26.304
1000	381.58	719.31	−249.58	531.33	−27.752
		2,3-Dimethylpentane C_7H_{16}			
300	166.77	415.09	−199.49	1.88	−0.330
400	210.96	469.24	−211.04	70.84	−9.251
500	251.33	520.74	−220.58	142.47	−14.881
600	285.89	569.69	−228.19	215.77	−18.783
700	315.39	616.05	−233.97	290.29	−21.660
800	340.70	659.82	−238.24	365.43	−23.858
900	362.67	701.28	−241.08	441.08	−25.599
1000	381.58	740.48	−242.67	517.06	−27.006
		2,4-Dimethylpentane C_7H_{16}			
300	166.77	397.69	−202.25	4.35	−0.758
400	210.96	451.83	−213.80	75.06	−9.800
500	251.33	503.34	−223.34	148.41	−15.502
600	285.89	552.29	−230.96	223.47	−19.452
700	315.39	598.65	−236.73	299.70	−22.363
800	340.70	642.41	−241.00	376.56	−24.587
900	362.67	683.87	−243.84	454.01	−26.348
1000	381.58	723.08	−245.43	531.70	−27.771
		3,3-Dimethylpentane C_7H_{16}			
300	166.77	400.74	−201.79	3.89	−0.678
400	210.96	454.88	−213.34	74.27	−9.700
500	251.33	506.39	−222.88	147.32	−15.390
600	285.89	555.34	−230.50	222.09	−19.333
700	315.39	601.70	−236.27	298.03	−22.237
800	340.70	645.47	−240.54	374.59	−24.457
900	362.67	686.93	−243.38	451.70	−26.215
1000	381.58	726.13	−244.97	529.12	−27.636
		2,2,3-Trimethylbutane C_7H_{16}			
300	165.44	384.34	−205.06	5.56	−0.967
400	212.67	438.53	−216.56	77.57	−10.131
500	255.39	490.70	−225.81	152.26	−15.903
600	291.25	540.49	−232.92	228.53	−19.893
700	321.08	587.68	−238.15	305.89	−22.825
800	346.14	632.24	−241.88	383.84	−25.060
900	367.69	674.29	−244.22	462.25	−26.826
1000	386.27	714.04	−245.35	540.87	−28.250

Table A.21 (*continued*)

T, K	C_p, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Octane C_8H_{18}			
300	189.74	467.90	−208.74	17.78	−3.093
400	240.00	529.49	−221.58	95.31	−12.445
500	285.85	588.10	−232.21	175.81	−18.364
600	324.97	643.75	−240.62	258.19	−22.475
700	358.40	696.43	−247.02	341.87	−25.511
800	387.02	746.17	−251.71	426.27	−27.832
900	411.83	793.24	−254.81	511.28	−29.672
1000	433.46	837.76	−256.44	596.55	−31.160
		2-Methylheptane C_8H_{18}			
300	189.74	456.43	−215.77	14.18	−2.468
400	239.99	518.02	−228.61	92.84	−12.125
500	285.85	576.64	−239.24	174.51	−18.228
600	324.97	632.29	−247.65	258.03	−22.462
700	358.40	684.96	−254.05	342.88	−25.585
800	387.02	734.71	−258.74	428.44	−27.972
900	411.83	781.78	−261.83	514.55	−29.863
1000	433.46	826.30	−263.47	600.99	−31.391
		3-Methylheptane C_8H_{18}			
300	189.74	462.75	−212.92	15.15	−2.634
400	239.99	524.34	−225.77	93.18	−12.167
500	285.85	582.96	−236.40	174.18	−18.196
600	324.97	638.60	−244.81	257.06	−22.380
700	358.40	691.28	−251.21	341.29	−25.467
800	387.02	741.03	−255.89	426.22	−27.828
900	411.83	788.10	−258.99	511.75	−29.698
1000	433.46	832.62	−260.62	597.52	−31.210
		4-Methylheptane C_8H_{18}			
300	189.74	454.51	−212.38	18.16	−3.159
400	239.99	516.10	−225.22	97.03	−12.669
500	285.85	574.71	−235.85	178.87	−18.683
600	324.97	630.36	−244.26	262.59	−22.858
700	358.40	683.04	−250.66	347.61	−25.938
800	387.02	732.79	−255.35	433.34	−28.294
900	411.83	779.86	−258.45	519.69	−30.161
1000	433.46	824.37	−260.08	606.30	−31.669
		3-Ethylhexane C_8H_{18}			
300	189.74	459.36	−211.17	17.91	−3.117
400	239.99	520.95	−224.01	96.27	−12.573
500	285.85	579.57	−234.64	177.65	−18.556
600	324.97	635.21	−243.05	260.87	−22.710
700	358.40	687.89	−249.45	345.43	−25.775
800	387.02	737.64	−254.14	430.70	−28.119
900	411.83	784.71	−257.23	516.51	−29.977
1000	433.46	829.23	−258.86	602.66	−31.479

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		2,2-Dimethylhexane C_8H_{18}			
300	189.74	432.37	−225.02	12.13	−2.115
400	239.99	493.96	−237.86	93.22	−12.175
500	285.85	552.58	−248.49	177.28	−18.519
600	324.97	608.23	−256.90	263.22	−22.914
700	358.40	660.90	−263.30	350.49	−26.152
800	387.02	710.65	−267.99	438.44	−28.625
900	411.83	757.72	−271.08	526.97	−30.583
1000	433.46	802.24	−272.71	615.80	−32.165
		2,3-Dimethylhexane C_8H_{18}			
300	189.74	445.14	−214.22	19.12	−3.328
400	239.99	506.72	−227.07	98.91	−12.918
500	285.85	565.34	−237.69	181.71	−18.980
600	324.97	620.99	−246.10	266.35	−23.187
700	358.40	673.67	−252.50	352.33	−26.290
800	387.02	723.41	−257.19	439.03	−28.663
900	411.83	770.48	−260.29	526.26	−30.543
1000	433.46	815.00	−261.92	613.83	−32.062
		2,4-Dimethylhexane C_8H_{18}			
300	189.74	446.81	−219.70	13.14	−2.286
400	239.99	508.40	−232.55	92.76	−12.115
500	285.85	567.02	−243.17	175.39	−18.320
600	324.97	622.66	−251.58	259.87	−22.623
700	358.40	675.34	−257.99	345.68	−25.794
800	387.02	725.09	−262.67	432.21	−28.218
900	411.83	772.16	−265.77	519.28	−30.138
1000	433.46	816.67	−267.40	606.68	−31.689
		2,5-Dimethylhexane C_8H_{18}			
300	189.74	440.20	−222.92	11.88	−2.071
400	239.99	501.79	−235.77	92.22	−12.039
500	285.85	560.40	−246.40	175.48	−18.329
600	324.97	616.05	−254.81	260.62	−22.687
700	358.40	668.73	−261.21	347.10	−25.899
800	387.02	718.48	−265.89	434.26	−28.353
900	411.83	765.55	−268.99	522.04	−30.296
1000	433.46	810.06	−270.62	610.07	−31.866
		3,3-Dimethylhexane C_8H_{18}			
300	189.74	439.24	−220.41	14.69	−2.558
400	239.99	500.82	−233.26	95.10	−12.417
500	285.85	559.44	−243.89	178.45	−18.642
600	324.97	615.09	−252.30	263.72	−22.956
700	358.40	667.77	−258.70	350.28	−26.137
800	387.02	717.51	−263.38	437.52	−28.567
900	411.83	764.58	−266.48	525.38	−30.492
1000	433.46	809.10	−268.11	613.54	−32.047

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		3,4-Dimethylhexane C_8H_{18}			
300	189.74	449.49	−213.30	18.74	−3.261
400	239.99	511.08	−226.15	98.11	−12.811
500	285.85	569.69	−236.77	180.46	−18.849
600	324.97	625.34	−245.18	264.68	−23.040
700	358.40	678.02	−251.58	350.20	−26.132
800	387.02	727.76	−256.27	436.43	−28.496
900	411.63	774.83	−259.37	523.29	−30.369
1000	433.46	819.35	−261.00	610.40	−31.883
		3-Ethyl-2-methylpentane C_8H_{18}			
300	189.74	442.29	−211.50	22.68	−3.950
400	239.99	503.88	−224.35	102.80	−13.421
500	285.85	562.50	−234.97	185.85	−19.413
600	324.97	618.14	−243.38	270.79	−23.573
700	358.40	670.82	−249.78	357.06	−26.642
800	387.02	720.57	−254.47	444.01	−28.989
900	411.83	767.64	−257.57	531.58	−30.850
1000	433.46	812.16	−259.20	619.40	−32.353
		3-Ethyl-3-methylpentane C_8H_{18}			
300	189.74	434.13	−215.27	21.38	−3.721
400	239.99	495.72	−228.11	102.30	−13.356
500	285.85	554.34	−238.74	186.15	−19.446
600	324.97	609.99	−247.15	271.92	−23.671
700	358.40	662.66	−253.55	358.99	−26.787
800	387.02	712.41	−258.24	446.77	−29.170
900	411.83	759.48	−261.33	535.13	−31.057
1000	433.46	804.00	−262.96	623.79	−32.582
		2,2,3-Trimethylpentane C_8H_{18}			
300	189.74	426.35	−220.41	18.58	−3.231
400	239.99	487.94	−233.26	100.25	−13.090
500	285.85	546.56	−243.89	184.89	−19.315
600	324.97	606.39	−252.30	271.42	−23.629
700	358.40	654.88	−258.70	359.28	−26.810
800	387.02	704.63	−263.38	447.86	−29.240
900	411.83	751.70	−266.48	537.02	−31.165
1000	433.46	796.22	−268.11	626.43	−32.720
		2,2,4-Trimethylpentane C_8H_{18}			
300	189.74	424.38	−224.43	15.15	−2.634
400	239.99	485.97	−237.27	97.03	−12.669
500	285.85	544.59	−247.90	181.88	−18.998
600	324.97	600.24	−256.31	268.61	−23.382
700	358.40	652.91	−262.71	356.64	−26.613
800	387.02	702.66	−267.40	445.39	−29.081
900	411.83	749.73	−270.50	534.76	−31.035
1000	433.46	794.25	−272.13	624.38	−32.613

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		2,3,4-Trimethylpentane C_8H_{18}			
300	189.74	432.71	−216.73	20.33	−3.540
400	239.99	494.30	−229.58	101.38	−13.239
500	285.85	552.92	−240.20	185.39	−19.367
600	324.97	608.56	−248.61	271.29	−23.618
700	358.40	661.24	−255.01	358.53	−26.752
800	387.02	710.99	−259.70	446.43	−29.148
900	411.83	758.06	−262.80	534.97	−31.047
1000	433.46	802.57	−264.43	623.75	−32.580
		2,3,3-Trimethylpentane C_8H_{18}			
300	189.74	429.24	−217.74	20.38	−3.546
400	239.99	490.83	−230.58	101.75	−13.289
500	285.85	549.44	−241.21	186.15	−19.444
600	324.97	605.09	−249.62	272.38	−23.712
700	358.40	657.77	−256.02	359.95	−26.859
800	387.02	707.51	−260.71	448.23	−29.264
900	411.83	754.58	−263.80	537.06	−31.170
1000	433.46	799.10	−265.43	626.22	−32.709
		2,2,3,3-Tetramethylbutane C_8H_{18}			
300	193.68	390.58	−226.15	23.51	−4.096
400	250.54	454.26	−238.28	108.70	−14.194
500	300.24	515.68	−247.65	196.56	−20.535
600	341.08	574.13	−254.51	286.06	−24.903
700	374.55	629.27	−259.28	376.56	−28.101
800	402.42	681.16	−262.38	467.60	−30.530
900	425.93	729.94	−264.01	559.02	−32.443
1000	446.01	775.92	−264.35	650.57	−33.980
		Nonane C_9H_{20}			
300	212.76	507.02	−229.33	26.36	−4.593
400	269.03	576.05	−243.55	113.85	−14.869
500	320.33	641.75	−255.22	204.60	−21.375
600	364.05	704.08	−264.47	297.44	−25.894
700	401.37	763.08	−271.46	391.71	−29.229
800	433.30	818.81	−276.56	486.77	−31.880
900	460.95	871.49	−279.91	582.45	−33.802
1000	484.93	921.32	−281.63	678.44	−35.486
		Decane $C_{10}H_{22}$			
300	235.73	546.10	−249.99	34.94	−6.085
400	298.07	622.58	−265.52	132.38	−17.287
500	354.85	695.38	−278.28	233.38	−24.381
600	403.17	764.42	−288.36	336.69	−29.308
700	444.38	829.77	−295.93	441.54	−32.945
800	479.61	891.44	−301.46	547.18	−35.725
900	510.11	949.73	−305.01	653.54	−37.929
1000	536.39	1004.87	−306.81	760.23	−39.709

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Undecane $C_{11}H_{24}$			
300	258.74	585.22	−270.66	43.51	−7.576
400	327.11	669.15	−287.52	150.92	−19.706
500	389.32	748.98	−301.33	262.17	−27.387
600	442.25	824.79	−312.25	375.89	−32.722
700	487.35	896.42	−320.41	491.33	−36.660
800	525.89	964.08	−326.25	607.60	−39.671
900	559.23	1027.97	−330.16	724.67	−42.056
1000	588.27	1088.43	−332.04	842.07	−43.983
		Dodecane $C_{12}H_{26}$			
300	281.71	624.25	−291.25	52.13	−9.078
400	356.18	715.67	−309.45	169.49	−22.132
500	423.84	802.62	−324.34	291.00	−30.400
600	481.33	885.08	−336.10	415.18	−36.142
700	530.36	963.07	−344.85	541.16	−40.381
800	572.20	1036.67	−351.16	668.10	−43.621
900	608.40	1106.21	−355.22	795.84	−46.188
1000	639.73	1171.98	−357.19	923.95	−48.260
		Tridecane $C_{13}H_{28}$			
300	304.68	663.33	−311.92	60.71	−10.570
400	385.22	762.20	−331.46	188.03	−24.551
500	458.36	856.21	−347.40	319.78	−33.406
600	520.41	945.42	−359.95	454.38	−39.557
700	573.33	1029.72	−369.32	590.99	−44.097
800	618.48	1109.30	−376.06	728.52	−47.566
900	657.56	1184.45	−380.37	866.97	−50.315
1000	691.20	1255.53	−382.42	1005.79	−52.534
		Tetradecane $C_{14}H_{30}$			
300	327.69	702.45	−332.59	69.29	−12.062
400	414.26	808.77	−353.42	206.52	−26.970
500	493.67	909.85	−370.49	348.57	−36.413
600	559.48	1005.75	−383.84	493.63	−46.386
700	616.35	1096.38	−393.84	640.78	−51.528
800	664.80	1181.94	−400.95	788.98	−55.457
900	706.68	1262.69	−405.47	938.05	−58.569
1000	743.08	1339.09	−407.61	1087.59	−61.081
		Pentadecane $C_{15}H_{32}$			
300	350.66	741.53	−353.21	77.86	−13.554
400	443.29	855.29	−375.43	225.06	−29.389
500	527.35	963.49	−393.54	377.35	−39.419
600	598.60	1066.08	−407.73	532.83	−46.386
700	659.36	1163.07	−418.32	690.57	−51.528
800	711.07	1254.57	−425.85	849.39	−55.457
900	755.84	1340.93	−430.62	1009.18	−58.569
1000	794.54	1422.64	−432.79	1169.43	−61.081

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Hexadecane $C_{16}H_{34}$			
300	373.67	780.65	−373.84	86.44	−15.053
400	472.33	901.86	−397.35	243.63	−31.813
500	561.83	1017.13	−416.56	406.18	−42.430
600	637.68	1126.46	−431.58	572.12	−49.804
700	702.33	1229.72	−442.75	740.40	−55.246
800	757.39	1327.16	−450.70	909.85	−59.405
900	804.96	1419.21	−455.72	1080.35	−62.699
1000	846.00	1506.20	−457.98	1251.27	−65.357
		Eicosane $C_{20}H_{42}$			
300	465.60	937.01	−456.39	120.83	−21.035
400	588.48	1088.05	−485.22	317.82	−41.499
500	699.86	1231.64	−508.69	521.37	−54.464
600	794.04	1367.79	−527.02	729.06	−63.469
700	874.33	1496.37	−540.57	939.64	−70.115
800	942.57	1617.70	−550.20	1151.65	−75.192
900	1001.57	1732.18	−556.14	1364.86	−79.212
1000	1052.69	1840.42	−558.69	1578.62	−82.456
		Cycloalkanes			
		Cyclopropane C_3H_6			
300	56.23	237.82	53.18	104.72	−18.232
400	76.61	256.81	48.03	122.72	−16.023
500	94.77	275.93	43.89	141.88	−14.821
600	109.41	294.55	40.58	161.80	−14.084
700	121.42	312.34	38.03	182.21	−13.596
800	131.59	329.24	36.02	202.92	−13.249
900	140.46	345.26	34.60	223.89	−12.994
1000	148.07	360.45	33.68	245.02	−12.797
		Cyclobutane C_4H_8			
300	72.68	265.85	26.48	110.58	−19.250
400	99.96	290.58	19.41	139.70	−18.243
500	124.93	315.64	13.68	170.46	−17.808
600	145.44	340.28	9.16	202.25	−17.607
700	162.72	364.00	5.77	234.72	−17.516
800	177.49	386.73	3.26	267.61	−17.471
900	190.00	408.40	1.63	300.75	−17.455
1000	200.66	428.99	0.71	334.09	−17.450
		Cycloheptane C_7H_{14}			
300	124.06	343.13	−119.58	64.14	−11.168
400	174.97	385.89	−132.17	127.40	−16.635
500	221.50	430.07	−142.09	193.47	−20.212
600	261.17	474.05	−149.45	261.29	−22.746
700	294.39	516.85	−154.60	330.20	−24.640
800	322.29	558.06	−157.86	399.66	−26.094
900	345.81	597.39	−159.54	469.49	−27.248
1000	365.68	634.88	−159.75	539.44	−28.177

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Cyclooctane C_8H_{16}			
300	141.04	367.65	−126.06	91.25	−15.888
400	200.08	416.48	−140.46	165.98	−21.675
500	252.76	466.93	−151.80	243.97	−25.486
600	297.06	517.06	−160.33	323.93	−28.199
700	334.09	565.68	−166.40	405.18	−30.234
800	365.26	612.37	−170.41	487.06	−31.801
900	391.71	656.97	−172.63	569.44	−33.048
1000	414.26	699.44	−173.22	651.99	−34.055
		Spiropentane C_5H_8			
300	88.66	282.80	185.10	265.81	−46.277
400	119.45	312.59	178.74	293.72	−38.354
500	146.06	342.21	173.72	323.05	−33.749
600	167.78	370.83	169.83	353.30	−30.755
700	185.60	398.07	166.90	384.13	−28.663
800	200.46	423.84	164.81	415.30	−27.114
900	213.09	448.19	163.39	446.73	−25.925
1000	223.89	471.20	162.67	478.27	−24.981
		Cyclopentanes			
		Cyclopentane C_5H_{10}			
300	83.64	293.42	−77.45	39.33	−6.844
400	118.74	322.34	−86.99	79.75	−10.412
500	150.92	352.42	−94.73	122.34	−12.780
600	178.11	382.38	−100.79	166.31	−14.480
700	200.87	411.58	−105.35	211.25	−15.763
800	220.08	439.70	−108.66	256.69	−16.759
900	236.40	466.60	−110.88	302.50	−17.557
1000	250.37	492.25	−112.13	348.57	−18.206
		Methylcyclopentane C_6H_{12}			
300	110.71	340.62	−106.90	36.61	−6.377
400	151.08	378.07	−117.40	86.15	−11.248
500	188.03	415.85	−125.94	138.07	−14.421
600	219.37	453.00	−132.59	191.46	−16.669
700	245.52	488.82	−137.57	245.94	−18.351
800	267.78	523.08	−141.13	300.91	−19.648
900	286.73	555.76	−143.47	356.35	−20.682
1000	303.09	586.85	−144.64	412.00	−21.521
		Ethylcyclopentane C_7H_{14}			
300	132.84	379.15	−127.32	45.61	−7.941
400	183.64	424.63	−138.95	105.10	−13.726
500	221.88	469.74	−148.45	167.28	−17.473
600	258.15	513.50	−155.98	231.12	−20.119
700	288.78	555.64	−161.54	296.10	−22.096
800	314.72	595.93	−165.48	361.71	−23.617
900	336.98	634.34	−167.95	427.81	−24.829
1000	356.31	670.86	−169.08	494.13	−25.810

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1,1-Dimethylcyclopentane C_7H_{14}			
300	134.56	360.12	−138.53	40.12	−6.983
400	182.21	404.22	−150.21	101.50	−13.256
500	225.98	450.95	−159.54	165.56	−17.296
600	262.67	495.47	−166.61	231.25	−20.132
700	293.21	538.36	−171.75	298.03	−22.238
800	318.74	579.19	−175.27	365.35	−23.853
900	340.49	618.02	−177.36	433.09	−25.135
1000	359.11	654.88	−178.15	501.03	−26.169
		cis-1,2-Dimethylcyclopentane C_7H_{14}			
300	135.31	366.98	−129.79	46.78	−8.148
400	182.72	412.50	−141.42	107.49	−14.038
500	226.06	458.06	−150.71	170.83	−17.847
600	262.42	502.58	−157.79	235.81	−20.529
700	292.55	545.38	−162.97	301.88	−22.526
800	317.90	586.14	−166.57	368.48	−24.060
900	339.49	624.84	−168.74	435.55	−25.278
1000	358.02	661.62	−169.66	502.83	−26.263
		trans-1,2-Dimethylcyclopentane C_7H_{14}			
300	135.73	367.65	−136.94	39.46	−6.867
400	182.88	413.25	−148.53	100.08	−13.068
500	226.06	458.86	−157.82	163.34	−17.063
600	262.17	503.34	−164.93	228.24	−19.869
700	292.38	546.10	−170.12	294.22	−21.955
800	317.31	585.81	−173.76	360.79	−23.555
900	338.82	625.47	−175.98	427.77	−24.826
1000	357.44	662.12	−176.98	494.97	−25.854
		cis-1,3-Dimethylcyclopentane C_7H_{14}			
300	135.73	367.65	−136.11	40.29	−7.013
400	182.88	413.25	−147.70	100.92	−13.177
500	226.06	458.86	−156.98	164.18	−17.151
600	262.17	503.34	−164.10	229.07	−19.942
700	292.38	546.10	−169.28	295.06	−22.018
800	317.31	586.81	−172.92	361.62	−23.610
900	338.82	625.47	−175.14	428.61	−24.875
1000	357.44	662.12	−176.15	495.80	−25.897
		trans-1,3-Dimethylcyclopentane C_7H_{14}			
300	135.73	367.65	−133.85	42.55	−7.406
400	182.88	413.25	−145.44	103.18	−13.472
500	226.06	458.86	−154.72	166.44	−17.387
600	262.17	503.34	−161.84	231.33	−20.139
700	292.38	546.10	−167.03	297.32	−22.186
800	317.31	586.81	−170.67	363.88	−23.758
900	338.82	625.47	−172.88	430.87	−25.006
1000	357.44	662.12	−173.89	498.06	−26.015

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Propylcyclopentane C_8H_{16}			
300	155.81	418.23	−148.36	53.81	−9.368
400	212.67	471.16	−161.34	123.26	−16.095
500	256.40	523.38	−171.88	195.64	−20.440
600	297.23	573.84	−180.25	269.95	−23.500
700	331.79	622.33	−186.40	345.56	−25.783
800	361.00	668.56	−190.75	421.79	−27.538
900	386.14	712.58	−193.47	498.57	−28.934
1000	407.94	754.42	−194.68	575.59	−30.064
		Butylcyclopentane C_9H_{18}			
300	178.82	457.35	−168.57	62.80	−10.933
400	241.71	517.73	−182.88	142.21	−18.569
500	290.87	577.02	−194.51	224.85	−23.490
600	336.31	634.17	−203.68	309.57	−26.951
700	376.76	688.98	−210.46	395.76	−29.530
800	407.31	741.20	−215.22	482.62	−31.511
900	435.26	790.61	−218.36	570.11	−33.086
1000	480.32	838.64	−218.78	657.75	−34.360
		1-Cyclopentylpentane $C_{10}H_{20}$			
300	201.79	496.43	−189.24	71.38	−12.424
400	270.75	564.30	−204.89	160.71	−20.987
500	325.39	630.65	−217.57	253.63	−26.496
600	375.43	694.50	−227.57	348.82	−30.366
700	417.77	755.67	−234.93	455.55	−33.245
800	453.63	813.83	−240.12	543.04	−35.456
900	484.42	869.10	−243.30	641.20	−37.213
1000	511.28	921.53	−244.64	739.65	−38.633
		1-Cyclopentylhexane $C_{11}H_{22}$			
300	224.81	535.55	−209.87	79.96	−13.924
400	299.78	610.82	−226.81	179.28	−23.412
500	359.87	684.29	−240.58	282.46	−29.507
600	414.51	754.84	−251.42	388.07	−33.784
700	460.74	822.32	−259.37	495.39	−36.964
800	499.90	886.46	−264.97	603.54	−39.404
900	533.54	947.30	−268.40	712.37	−41.342
1000	562.75	1005.08	−269.83	821.49	−42.909
		1-Cyclopentylheptane $C_{12}H_{24}$			
300	247.78	574.59	−230.50	88.53	−15.418
400	328.86	657.35	−248.78	197.82	−25.832
500	394.38	737.89	−263.63	311.25	−32.515
600	453.59	815.17	−275.31	427.31	−37.200
700	503.75	888.93	−283.84	545.22	−40.681
800	546.18	959.06	−289.87	663.96	−43.351
900	582.71	1025.54	−293.51	783.50	−45.471
1000	614.21	1088.59	−295.01	903.37	−47.184

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1-Cyclopentyloctane $C_{13}H_{26}$			
300	270.75	613.67	−251.12	97.15	−16.917
400	357.90	703.87	−270.75	216.40	−28.257
500	428.90	791.53	−286.65	340.08	−35.526
600	492.67	875.50	−299.16	466.60	−40.618
700	546.77	955.63	−308.28	595.05	−44.400
800	592.50	1031.69	−314.68	724.46	−47.299
900	631.87	1103.78	−318.61	854.67	−49.601
1000	666.09	1172.19	−320.16	985.21	−51.460
		1-Cyclopentylnonane $C_{14}H_{28}$			
300	293.76	652.79	−271.79	105.73	−18.409
400	386.94	750.44	−292.71	234.93	−30.675
500	463.38	845.17	−309.74	368.86	−38.532
600	531.74	935.84	−323.00	505.80	−44.033
700	589.73	1022.28	−332.75	644.84	−48.116
800	638.81	1104.33	−339.57	784.88	−51.245
900	680.99	1182.02	−434.72	925.79	−53.728
1000	717.56	1255.74	−345.39	1067.05	−55.734
		1-Cyclopentyldecane $C_{15}H_{30}$			
300	316.73	691.87	−292.46	114.31	−19.901
400	415.97	797.01	−314.72	253.42	−33.094
500	497.90	898.77	−332.80	397.65	−41.538
600	570.86	996.17	−346.90	545.05	−47.447
700	632.75	1088.97	−357.23	694.63	−51.831
800	685.09	1176.96	−364.47	845.29	−55.190
900	730.15	1260.30	−368.86	996.88	−57.855
1000	769.02	1339.30	−370.58	1148.84	−60.007
		1-Cyclopentylundecane $C_{16}H_{32}$			
300	339.47	730.99	−313.05	122.93	−21.400
400	445.01	843.54	−336.64	272.00	−35.518
500	532.37	952.40	−355.81	426.43	−44.549
600	609.94	1056.50	−370.74	584.30	−50.865
700	675.72	1155.62	−381.71	744.46	−55.550
800	731.36	1249.55	−389.32	905.79	−59.138
900	779.27	1338.55	−393.97	1068.05	−61.985
1000	820.90	1422.85	−395.76	1230.72	−64.283
		Cyclohexanes			
		Cyclohexane C_6H_{12}			
300	107.03	298.90	−123.34	32.68	−5.691
400	149.87	335.64	−134.14	86.39	−11.284
500	190.25	373.51	−142.59	146.55	−14.893
600	225.22	411.37	−148.82	200.20	−17.428
700	254.68	448.36	−153.05	258.74	−19.308
800	279.32	448.05	−155.60	317.73	−20.745
900	299.91	518.15	−156.69	377.02	−21.880
1000	317.15	550.66	−156.48	436.35	−22.791

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Methylcyclohexane C_7H_{14}			
300	136.02	344.22	−155.02	28.40	−4.946
400	185.56	390.20	−166.44	91.38	−11.932
500	230.99	436.64	−175.35	156.90	−16.391
600	269.70	482.25	−181.84	223.97	−19.498
700	302.21	526.35	−186.15	292.00	−21.789
800	329.45	568.52	−188.69	360.45	−23.534
900	352.29	608.69	−189.66	429.19	−24.909
1000	371.50	646.80	−189.24	498.02	−26.012
		Ethylcyclohexane C_8H_{16}			
300	159.95	383.59	−172.05	40.54	−7.056
400	215.89	437.40	−184.68	113.39	−14.808
500	266.94	491.20	−194.51	189.12	−19.756
600	310.03	543.75	−201.71	266.52	−23.201
700	346.44	594.38	−206.48	345.01	−25.743
800	376.98	642.66	−209.28	429.92	−27.679
900	402.50	688.60	−210.41	503.21	−29.204
1000	423.84	732.16	−209.99	582.54	−30.428
		1,1-Dimethylcyclohexane C_8H_{16}			
300	155.64	365.97	−181.29	36.57	−6.364
400	212.13	418.61	−194.35	111.25	−14.527
500	264.85	471.75	−204.47	188.87	−19.731
600	310.03	524.13	−211.75	268.24	−23.351
700	348.10	574.84	−216.48	348.69	−26.018
800	379.49	623.46	−219.07	429.57	−28.046
900	405.85	669.69	−219.87	510.74	−29.641
1000	427.60	713.62	−219.07	591.95	−30.919
		***cis*-1,2-Dimethylcyclohexane C_8H_{16}**			
300	157.74	375.51	−172.46	42.55	−7.405
400	213.80	428.65	−185.35	116.23	−15.180
500	265.68	482.08	−195.35	192.84	−20.146
600	309.62	534.51	−202.59	271.17	−23.607
700	346.44	585.09	−207.40	350.58	−26.160
800	376.98	633.42	−210.20	430.45	−28.104
900	402.92	679.36	−211.29	510.66	−29.636
1000	424.26	722.95	−210.83	590.91	−30.865
		***trans*-1,2-Dimethylcyclohexane C_8H_{16}**			
300	160.25	371.92	−180.29	35.77	−6.231
400	217.15	425.93	−192.84	109.83	−14.340
500	268.61	480.07	−202.55	186.65	−19.499
600	312.13	532.99	−209.53	265.14	−23.083
700	348.53	583.92	−214.09	344.72	−25.721
800	378.65	632.49	−216.73	424.68	−27.726
900	404.17	678.60	−217.65	504.97	−29.305
1000	425.51	722.33	−217.07	585.26	−30.570

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		cis-1,3-Dimethylcyclohexane C_8H_{16}			
300	158.57	371.46	−185.06	31.17	−5.425
400	214.22	424.76	−197.86	105.27	−13.746
500	266.10	478.31	−207.82	182.26	−19.039
600	310.45	530.82	−215.02	260.96	−22.717
700	347.69	581.58	−219.70	340.74	−25.424
800	378.65	630.07	−222.38	420.31	−27.483
900	404.59	676.22	−223.30	501.45	−29.102
1000	426.77	720.02	−224.63	582.04	−30.400
		trans-1,3-Dimethylcyclohexane C_8H_{16}			
300	158.57	377.23	−176.86	37.61	−6.551
400	213.80	430.49	−189.70	111.17	−14.515
500	265.27	483.88	−199.70	187.57	−19.596
600	308.78	536.18	−207.02	265.73	−23.133
700	345.18	586.60	−211.92	344.97	−25.742
800	375.72	634.75	−214.89	424.72	−27.729
900	401.25	680.53	−216.10	504.80	−29.295
1000	423.00	723.96	−215.81	584.92	−30.552
		cis-1,4-Dimethylcyclohexane C_8H_{16}			
300	158.57	371.46	−176.94	39.29	−6.838
400	213.80	424.72	−189.69	113.39	−14.806
500	265.27	478.11	−199.79	190.37	−19.889
600	308.78	530.41	−207.11	269.11	−23.427
700	345.18	580.82	−212.00	348.95	−26.037
800	375.72	628.98	−214.97	429.24	−28.025
900	401.25	674.75	−216.19	509.90	−29.592
1000	423.00	718.18	−215.89	590.61	−30.849
		trans-1,4-Dimethylcyclohexane C_8H_{16}			
300	158.99	365.81	−184.89	33.01	−5.749
400	215.89	419.45	−197.57	107.70	−14.061
500	267.78	473.36	−207.36	185.18	−19.345
600	312.13	526.22	−214.39	264.35	−23.013
700	348.53	577.14	−218.99	344.59	−25.712
800	379.07	625.72	−221.58	425.22	−27.763
900	405.01	671.91	−222.46	506.18	−29.377
1000	426.35	715.92	−221.75	587.18	−30.669
		Propylcyclohexane C_9H_{18}			
300	185.43	420.70	−193.59	48.79	−8.493
400	247.27	482.62	−207.36	131.75	−17.207
500	303.76	544.05	−218.03	217.82	−22.756
600	350.62	603.71	−225.85	305.72	−26.616
700	390.37	660.82	−231.08	394.84	−29.461
800	423.42	715.17	−234.26	484.42	−31.628
900	451.04	766.68	−235.60	574.38	−33.335
1000	474.47	815.42	−235.36	664.46	−34.706

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		cis,cis-1,3,5-Trimethylcyclohexane C_9H_{18}			
300	181.13	391.50	−215.69	35.44	−6.170
400	242.88	452.16	−229.91	121.42	−15.854
500	301.21	512.75	−240.91	210.58	−21.998
600	351.20	572.26	−248.82	301.62	−26.258
700	393.17	629.61	−253.93	399.84	−29.388
800	427.86	684.42	−256.73	486.52	−31.766
900	456.89	736.55	−257.57	579.57	−33.635
1000	482.04	786.01	−256.65	672.58	−35.131
		cis,trans-1,3,5-Trimethylcyclohexane C_9H_{18}			
300	181.13	401.12	−206.86	41.38	−7.204
400	242.04	461.66	−221.12	126.40	−16.505
500	299.53	521.99	−232.25	214.64	−22.420
600	347.86	581.03	−240.41	304.76	−26.531
700	388.15	637.77	−245.94	396.14	−29.559
800	422.00	691.87	−249.28	488.06	−31.864
900	450.20	743.20	−250.96	580.36	−33.682
1000	474.51	791.95	−250.54	672.79	−35.140
		Butylcyclohexane $C_{10}H_{20}$			
300	208.41	459.78	−213.51	58.12	−10.116
400	276.14	529.15	−228.61	151.04	−19.724
500	338.97	597.64	−240.37	247.36	−25.842
600	389.53	663.92	−249.03	345.72	−30.097
700	433.46	727.39	−254.89	445.39	−33.235
800	469.86	787.68	−258.45	545.64	−35.624
900	500.41	844.83	−259.99	646.30	−37.503
1000	525.93	898.93	−259.83	747.09	−39.022
		Pentylcyclohexane $C_{11}H_{22}$			
300	231.42	498.90	−234.18	66.65	−11.608
400	305.43	575.76	−250.58	169.58	−22.142
500	372.79	651.37	−263.38	276.14	−28.847
600	428.86	724.42	−272.84	384.93	−33.510
700	476.56	794.21	−279.28	495.18	−36.948
800	515.89	860.48	−283.26	606.01	−39.566
900	549.36	933.20	−285.09	717.35	−41.632
1000	577.81	982.61	−284.97	828.81	−43.291
		1-Cyclohexylhexane $C_{12}H_{24}$			
300	254.39	537.98	−254.76	75.27	−13.107
400	334.30	622.29	−272.55	188.15	−24.567
500	407.52	704.96	−286.39	304.97	−31.859
600	467.77	784.71	−296.69	424.22	−36.929
700	519.23	860.82	−303.76	545.01	−40.667
800	562.33	933.03	−308.15	666.51	−43.515
900	598.31	1001.40	−310.20	788.52	−45.763
1000	629.27	1066.08	−310.20	910.73	−47.568

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1-Cyclohexylheptane $C_{13}H_{26}$			
300	277.40	577.06	−275.43	83.85	−14.599
400	363.59	668.85	−294.51	206.65	−26.985
500	441.83	758.64	−309.45	333.76	−34.864
600	507.10	845.13	−320.54	463.42	−40.342
700	562.33	927.55	−328.19	594.80	−44.381
800	608.35	1005.71	−333.00	726.89	−47.459
900	647.68	1079.72	−335.31	859.60	−49.888
1000	680.74	1149.72	−335.35	992.49	−51.840
		1-Cyclohexyloctane $C_{14}H_{28}$			
300	300.37	616.18	−296.06	92.47	−16.098
400	392.46	715.38	−316.44	225.22	−29.409
500	476.14	812.20	−332.46	362.59	−37.875
600	546.01	905.38	−344.43	502.71	−43.761
700	605.42	994.12	−352.67	644.63	−48.102
800	654.80	1078.26	−357.90	787.39	−51.409
900	697.05	1157.88	−360.41	930.81	−54.020
1000	732.20	1233.23	−360.54	1074.41	−56.118
		1-Cyclohexylnonane $C_{15}H_{30}$			
300	323.34	655.21	−316.69	101.04	−17.592
400	421.33	761.86	−338.44	243.76	−31.831
500	510.87	865.80	−355.56	391.37	−40.884
600	584.92	965.63	−368.32	541.95	−47.179
700	648.52	1060.73	−377.15	694.50	−51.820
800	701.24	1150.85	−382.79	847.89	−55.358
900	746.01	1236.08	−385.56	1001.98	−58.150
1000	784.08	1316.70	−385.76	1156.29	−60.395
		1-Cyclohexyldecane $C_{16}H_{32}$			
300	346.35	694.33	−337.36	109.62	−19.084
400	450.62	808.47	−350.41	262.29	−34.249
500	545.59	919.52	−378.57	420.16	−43.890
600	624.25	1026.13	−392.12	581.16	−50.591
700	691.62	1127.55	−401.54	744.25	−55.533
800	747.26	1223.61	−407.61	908.26	−59.299
900	794.96	1314.45	−410.62	1073.03	−62.273
1000	835.54	1400.38	−410.91	1238.00	−64.664
		Alkenes and Cycloalkenes			
		Ethylene (ethene) C_2H_4			
300	43.72	219.74	52.26	68.24	−11.879
400	53.97	233.76	49.25	74.01	−9.666
500	63.43	246.81	46.61	80.54	−8.412
600	71.55	259.12	44.35	87.53	−7.619
700	78.49	270.70	42.47	94.89	−7.079
800	84.52	281.58	40.88	102.47	−6.690
900	89.79	291.83	39.54	110.25	−6.399
1000	94.43	301.54	38.53	118.20	−6.173

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Propene C_3H_6			
300	64.18	267.36	20.33	62.97	−10.966
400	79.91	287.98	15.73	77.91	−10.175
500	94.64	307.44	11.72	93.93	−9.814
600	107.53	325.85	8.28	110.71	−9.638
700	118.70	343.30	5.48	128.03	−9.553
800	128.37	359.78	3.22	145.69	−9.511
900	136.82	375.43	1.46	163.59	−9.495
1000	144.18	390.20	0.17	181.71	−9.491
		1-Butene C_4H_8			
300	86.06	306.14	−0.25	71.71	−12.488
400	108.95	334.09	−6.23	96.65	−12.622
500	129.41	360.66	−11.30	122.97	−12.847
600	147.03	385.85	−15.52	150.25	−13.078
700	161.96	409.66	−18.87	178.15	−13.293
800	174.89	432.17	−21.51	206.44	−13.479
900	186.15	453.42	−23.51	235.10	−13.644
1000	195.89	473.55	−24.85	263.93	−13.786
		cis-2-Butene C_4H_8			
300	79.33	301.33	−7.11	66.27	−11.542
400	101.80	327.27	−13.81	91.80	−11.989
500	122.97	352.29	−19.58	118.91	−12.421
600	141.42	376.39	−24.35	147.03	−12.800
700	157.32	399.40	−28.24	175.94	−13.129
800	171.00	421.33	−31.34	205.31	−13.404
900	182.84	442.17	−33.68	235.06	−13.641
1000	193.09	462.00	−35.31	266.01	−13.843
		trans-2-Butene C_4H_8			
300	88.20	297.06	−11.30	63.42	−11.041
400	108.87	325.26	−17.20	89.24	−11.653
500	129.12	351.71	−27.61	116.44	−12.165
600	145.60	376.69	−31.71	144.60	−12.588
700	160.58	400.24	−35.02	173.49	−12.943
800	173.64	422.58	−37.66	202.71	−13.235
900	184.93	443.71	−39.62	232.30	−13.482
1000	194.89	463.71	−40.96	262.13	−13.692
		2-Methylpropene C_4H_8			
300	89.50	294.18	−17.03	58.53	−10.194
400	111.17	322.92	−22.72	84.64	−11.052
500	130.71	349.87	−27.61	112.05	−11.706
600	147.70	375.26	−31.71	140.37	−12.220
700	162.38	399.15	−35.02	169.33	−12.636
800	175.14	421.66	−37.66	198.70	−12.973
900	186.31	442.96	−39.62	228.40	−13.254

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1-Pentene C_5H_{10}			
300	110.08	346.52	−21.09	79.75	−13.885
400	138.49	382.12	−28.33	114.52	−14.951
500	164.14	415.85	−34.43	150.92	−15.766
600	186.44	447.81	−39.41	188.45	−16.406
700	205.27	477.98	−43.35	226.77	−16.922
800	221.54	506.47	−46.36	265.56	−17.388
900	235.64	533.42	−48.58	304.72	−17.684
1000	247.73	558.90	−49.96	344.09	−17.972
		cis-2-Pentene C_5H_{10}			
300	102.30	344.30	−28.24	72.47	−12.615
400	132.04	380.49	−36.19	107.28	−14.008
500	159.20	412.96	−42.84	143.93	−15.036
600	182.51	444.09	−48.28	181.79	−15.826
700	201.88	473.71	−52.59	220.54	−16.455
800	218.78	501.79	−55.94	259.74	−16.959
900	233.30	528.44	−58.37	299.37	−17.375
1000	245.94	553.67	−60.00	339.28	−17.720
		trans-2-Pentene C_5H_{10}			
300	108.95	341.12	−31.92	70.54	−12.28
400	136.69	376.31	−39.29	105.86	−13.821
500	162.13	409.62	−45.61	142.88	−14.925
600	184.18	441.16	−50.79	181.04	−15.761
700	203.09	470.99	−54.98	220.08	−16.420
800	219.45	499.19	−58.20	259.53	−16.946
900	233.68	525.89	−60.58	299.45	−17.378
1000	246.06	551.16	−62.17	339.57	−17.736
		2-Methyl-1-butene C_5H_{10}			
300	110.50	340.24	−36.48	66.23	−11.532
400	138.91	375.97	−43.68	101.59	−13.268
500	164.85	409.82	−49.71	138.66	−14.483
600	187.11	441.91	−54.64	176.77	−15.389
700	206.10	472.21	−58.49	215.69	−16.094
800	222.38	500.82	−61.46	255.01	−16.651
900	236.48	527.85	−63.55	294.76	−17.106
1000	248.66	553.42	−64.85	334.68	−17.480
		3-Methyl-1-butene C_5H_{10}			
300	119.12	334.22	−29.08	75.44	−13.131
400	147.52	372.50	−35.40	107.07	−14.528
500	171.42	408.02	−40.71	148.53	−15.518
600	192.05	441.16	−45.06	186.82	−16.262
700	209.83	472.12	−48.49	225.77	−16.845
800	225.31	501.16	−51.09	265.10	−17.307
900	238.61	528.48	−52.97	304.76	−17.686
1000	150.33	554.25	−54.10	344.59	−17.999

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		2-Methyl-2-butene C_5H_{10}			
300	105.52	339.24	−42.72	60.29	−10.497
400	133.60	373.51	−50.92	95.86	−12.514
500	159.28	406.14	−57.03	133.18	−12.913
600	181.67	437.19	−62.51	171.75	−14.950
700	201.00	466.68	−66.90	211.17	−15.756
800	217.78	494.63	−70.33	251.08	−16.393
900	232.30	521.16	−72.84	291.46	−16.914
1000	244.97	546.30	−74.56	332.04	−17.344
		1-Hexene C_6H_{12}			
300	132.97	385.47	−41.84	88.24	−15.361
400	167.49	428.53	−50.42	132.97	−17.360
500	198.61	469.32	−57.61	179.66	−18.766
600	225.52	507.98	−63.43	227.65	−19.817
700	248.29	544.51	−67.95	276.56	−20.636
800	267.86	578.94	−71.42	325.98	−21.282
900	284.76	611.49	−73.85	375.81	−21.811
1000	299.32	642.29	−75.31	425.93	−22.246
		cis-2-Hexene C_6H_{12}			
300	126.31	387.27	−52.55	77.03	−13.408
400	161.50	428.48	−61.76	121.63	−15.884
500	194.14	468.15	−69.45	168.41	−17.593
600	221.75	506.01	−75.69	216.56	−18.852
700	245.18	542.04	−80.54	265.68	−19.826
800	265.26	576.09	−84.27	315.39	−20.591
900	282.84	608.39	−86.94	365.56	−21.214
1000	297.90	638.98	−88.58	415.98	−21.726
		trans-2-Hexene C_6H_{12}			
300	132.97	381.46	−54.06	77.24	−13.444
400	166.10	424.30	−62.72	122.34	−15.976
500	197.07	464.76	−70.04	169.49	−17.705
600	223.43	503.08	−76.07	217.94	−18.973
700	246.44	539.32	−80.79	267.36	−19.950
800	266.10	573.54	−84.39	317.31	−20.717
900	282.84	605.84	−87.03	367.73	−21.341
1000	297.90	636.43	−88.66	418.40	−21.853
		cis-3-Hexene C_6H_{12}			
300	124.31	380.41	−47.82	83.81	−14.589
400	161.08	421.29	−57.15	129.12	−16.863
500	194.14	460.87	−64.85	176.65	−18.451
600	222.59	498.86	−71.04	225.52	−19.631
700	245.60	534.92	−75.86	275.35	−20.546
800	265.68	569.07	−79.54	325.72	−21.268
900	282.84	601.37	−82.17	376.60	−21.856
1000	297.90	631.99	−83.81	427.73	−22.340

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		trans-3-Hexene C_6H_{12}			
300	133.47	375.68	−54.60	78.41	−13.651
400	168.20	418.94	−63.14	124.10	−16.204
500	199.16	459.86	−70.25	171.75	−17.941
600	225.52	498.57	−76.02	220.66	−19.211
700	247.69	535.05	−80.58	270.54	−20.187
800	267.36	569.44	−84.10	320.91	−22.952
900	283.68	601.87	−86.61	371.71	−21.573
1000	298.74	632.58	−88.16	422.79	−22.082
		2-Methyl-1-pentene C_6H_{12}			
300	136.23	383.05	−52.43	78.37	−13.647
400	170.71	427.02	−60.67	123.30	−16.100
500	201.25	468.48	−67.57	170.12	−17.770
600	227.61	507.56	−73.18	218.15	−18.992
700	250.20	544.38	−77.49	267.11	−19.931
800	269.45	579.07	−80.75	316.52	−20.666
900	286.19	611.70	−83.01	366.35	−21.262
1000	300.41	642.70	−84.39	416.39	−21.750
		2-Methyl-2-pentene C_6H_{12}			
300	127.28	379.24	−59.96	72.01	−12.538
400	163.18	420.87	−68.99	117.44	−15.334
500	194.97	460.78	−76.61	164.93	−17.231
600	222.59	498.86	−82.72	213.80	−18.614
700	245.18	534.88	−87.57	263.68	−19.675
800	265.27	568.98	−91.29	314.05	−20.506
900	282.42	601.24	−93.97	364.93	−21.180
1000	297.48	631.78	−95.65	416.06	−21.732
		cis-3-Methyl-2-pentene C_6H_{12}			
300	127.28	379.24	−57.95	74.01	−12.888
400	163.18	420.87	−66.99	119.45	−15.596
500	194.97	460.78	−74.60	166.94	−17.440
600	222.59	498.86	−80.71	215.81	−18.789
700	245.18	534.88	−85.56	265.68	−19.824
800	265.27	568.98	−89.29	316.06	−20.637
900	282.42	601.24	−91.96	366.94	−21.296
1000	297.48	631.78	−93.64	418.07	−21.837
		trans-3-Methyl-2-pentene C_6H_{12}			
300	127.28	382.63	−58.87	72.09	−12.550
400	163.18	424.26	−67.91	117.15	−15.299
500	194.97	464.17	−75.52	164.35	−17.167
600	222.59	502.25	−81.63	212.88	−18.531
700	245.18	538.27	−86.48	262.38	−19.579
800	265.27	572.37	−90.21	312.46	−20.400
900	282.42	604.63	−92.88	362.96	−21.066
1000	297.48	635.17	−94.56	413.76	−21.612

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		3-Methyl-1-pentene C_6H_{12}			
300	143.05	377.73	−45.19	87.24	−15.187
400	177.82	423.76	−52.72	132.55	−17.311
500	207.53	466.73	−58.95	179.62	−18.765
600	232.63	506.81	−63.97	227.82	−19.831
700	253.97	544.30	−67.86	276.77	−20.653
800	272.80	579.48	−70.75	326.18	−21.297
900	288.40	612.53	−72.76	375.97	−21.819
1000	302.50	643.71	−73.89	421.75	−22.247
		4-Methyl-1-pentene C_6H_{12}			
300	127.36	368.53	−44.31	90.88	−15.822
400	162.76	410.12	−53.39	137.36	−17.937
500	199.14	449.91	−61.04	185.98	−19.426
600	221.33	487.77	−67.29	235.94	−20.539
700	244.35	523.63	−72.22	286.90	−21.408
800	264.01	557.60	−76.02	338.44	−22.096
900	280.75	589.65	−78.87	390.45	−22.660
1000	295.81	620.03	−80.71	442.75	−23.126
		cis-4-Methyl-2-pentene C_6H_{12}			
300	134.18	374.18	−50.50	82.97	−14.444
400	167.57	417.40	−59.04	128.78	−16.818
500	200.00	458.36	−66.15	176.61	−18.448
600	226.35	497.23	−71.84	225.68	−19.646
700	248.53	533.84	−76.32	275.68	−20.569
800	267.78	568.31	−79.75	326.14	−21.294
900	284.51	600.82	−82.22	377.06	−21.883
1000	299.16	631.57	−83.72	428.23	−22.367
		trans-4-Methyl-2-pentene C_6H_{12}			
300	142.00	369.15	−54.52	80.46	−14.009
400	175.31	414.68	−62.22	126.69	−16.541
500	204.18	456.98	−68.74	174.68	−18.247
600	229.28	496.47	−74.14	223.84	−19.488
700	251.04	533.50	−78.32	273.88	−20.437
800	269.87	568.27	−81.55	324.39	−21.180
900	286.19	601.03	−83.76	375.60	−21.781
1000	300.41	631.91	−85.14	426.43	−22.274
		2-Ethyl-1-butene C_6H_{12}			
300	134.22	377.44	−51.71	80.75	−14.062
400	170.29	421.12	−60.08	126.27	−16.487
500	201.67	462.58	−66.99	173.68	−18.142
600	228.02	501.75	−72.51	222.30	−19.352
700	250.20	538.61	−76.82	271.83	−20.283
800	269.45	573.29	−80.08	321.83	−21.012
900	286.19	606.01	−82.38	372.25	−21.603
1000	300.83	636.93	−83.68	422.88	−22.087

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		2,3-Dimethyl-1-butene C_6H_{12}			
300	144.10	366.56	−55.90	79.87	−13.906
400	178.24	412.79	−63.35	126.31	−16.494
500	207.12	455.76	−69.58	174.47	−18.226
600	231.79	495.76	−74.68	223.76	−19.478
700	253.13	533.13	−78.66	273.84	−20.433
800	271.96	568.19	−81.65	324.34	−21.177
900	287.86	601.16	−83.72	375.26	−21.779
1000	302.08	632.24	−84.89	426.39	−22.271
		3,3-Dimethyl-1-butene C_6H_{12}			
300	127.15	344.55	−43.35	99.04	−17.242
400	162.76	386.10	−52.43	147.90	−19.315
500	195.39	426.01	−60.00	198.91	−20.779
600	223.43	464.17	−66.11	251.25	−21.873
700	246.44	500.41	−70.84	304.60	−22.727
800	266.10	534.63	−74.43	358.40	−23.401
900	281.58	566.85	−77.11	412.71	−23.952
1000	297.06	597.35	−78.87	467.27	−24.407
		2,3-Dimethyl-2-butene C_6H_{12}			
300	124.18	365.43	−59.41	76.69	−13.354
400	156.82	405.64	−68.95	123.55	−16.135
500	188.45	444.09	−77.19	172.67	−18.038
600	216.65	480.99	−83.97	223.30	−19.438
700	241.29	516.31	−89.29	274.97	−20.517
800	262.67	549.94	−93.35	327.23	−21.366
900	281.37	581.99	−96.19	380.09	−22.055
1000	297.65	612.50	−97.95	433.09	−22.621
		1-Heptene C_7H_{14}			
300	155.94	424.59	−62.51	96.82	−16.853
400	196.52	475.09	−72.43	151.46	−19.779
500	233.13	522.96	−80.67	208.41	−21.773
600	264.60	568.31	−87.32	266.86	−23.231
700	291.29	511.16	−92.42	326.35	−24.351
800	314.13	551.57	−96.32	386.39	−25.228
900	333.93	689.77	−98.95	446.93	−24.938
1000	351.04	725.84	−100.50	507.73	−26.520
		1-Octene C_8H_{16}			
300	178.95	463.67	−83.18	105.35	−18.345
400	225.56	521.62	−94.39	170.00	−22.198
500	267.61	576.60	−103.72	237.19	−24.779
600	303.67	628.65	−111.21	306.10	−26.645
700	334.26	677.81	−116.94	375.14	−28.067
800	360.45	724.21	−121.21	446.81	−29.173
900	383.05	768.02	−124.10	518.63	−30.065
1000	402.50	809.39	−125.73	589.57	−30.794

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1-Nonene C_9H_{18}			
300	201.92	502.75	−103.76	113.97	−19.845
400	254.60	568.19	−116.36	188.57	−24.622
500	302.08	630.24	−126.73	266.02	−27.790
600	342.80	699.02	−135.06	345.35	−30.064
700	377.27	744.50	−141.38	425.97	−31.785
800	406.77	796.84	−146.02	507.31	−33.121
900	432.21	846.26	−149.16	589.19	−34.195
1000	453.96	892.95	−150.88	671.41	−35.069
		1-Decene $C_{10}H_{20}$			
300	224.93	541.87	−124.43	122.55	−21.336
400	289.63	614.76	−138.32	207.07	−27.041
500	336.60	683.87	−149.79	294.80	−30.796
600	381.87	749.35	−158.91	384.55	−33.478
700	420.24	811.15	−166.85	475.76	−35.501
800	453.04	869.48	−170.92	567.73	−37.067
900	481.33	924.50	−174.31	660.32	−38.322
1000	505.85	976.50	−176.10	753.25	−39.343
		1-Undecene $C_{11}H_{22}$			
300	247.90	579.40	−145.10	131.13	−22.228
400	312.71	661.28	−160.33	225.60	−29.459
500	371.12	737.51	−172.84	323.59	−33.802
600	420.95	809.69	−182.80	423.80	−36.892
700	463.25	877.85	−190.33	525.55	−39.216
800	499.32	942.11	−195.81	628.14	−41.012
900	530.49	1002.78	−199.41	731.45	−42.449
1000	557.31	1060.10	201.29	835.04	−43.616
		1-Dodecene $C_{12}H_{24}$			
300	270.87	619.99	−165.69	139.75	−24.330
400	341.75	707.81	−182.25	244.18	−31.886
500	405.64	791.11	−195.89	352.42	−36.815
600	460.03	869.98	−206.25	463.09	−40.313
700	506.26	944.45	−214.76	575.43	−42.937
800	545.64	1014.70	−220.66	688.64	−44.962
900	579.65	1080.98	−224.51	802.62	−46.581
1000	608.77	1143.61	−226.44	916.97	−47.894
		1-Tridecene $C_{13}H_{26}$			
300	293.88	659.11	−186.36	148.32	−25.822
400	370.79	754.36	−204.26	262.71	−33.304
500	440.11	844.75	−218.95	381.20	−39.822
600	499.11	930.31	−230.54	502.29	−43.727
700	549.23	1011.11	−239.24	625.22	−46.653
800	591.95	1087.34	−245.56	749.06	−48.907
900	628.77	1159.22	−249.62	873.74	−50.708
1000	660.24	1227.13	−251.67	998.76	−52.168

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1-Tetradecene $C_{14}H_{28}$			
300	316.85	698.18	−206.94	156.94	−27.328
400	399.82	800.90	−226.15	281.33	−36.734
500	474.63	898.39	−241.92	410.07	−42.837
600	538.23	990.69	−254.35	541.62	−47.149
700	592.25	1077.80	−263.63	675.09	−50.375
800	638.23	1159.97	−270.37	809.60	−52.858
900	677.93	1237.46	−274.68	944.91	−54.840
1000	712.12	1310.72	−275.77	1000.69	−56.446
		1-Pentadecene $C_{15}H_{30}$			
300	339.87	737.30	−227.69	165.44	−28.806
400	428.86	847.47	−248.24	299.74	−39.142
500	509.11	951.99	−265.06	438.73	−45.834
600	577.31	1051.02	−278.28	580.74	−50.556
700	635.21	1144.45	−288.19	724.84	−54.084
800	684.50	1232.56	−295.35	869.94	−56.798
900	727.05	1315.70	−299.91	1015.96	−58.962
1000	769.58	1394.28	−302.08	1162.40	−60.715
		1-Hexadecene $C_{16}H_{32}$			
300	362.84	776.38	−248.28	174.05	−30.305
400	457.90	894.00	−270.16	318.32	−41.566
500	543.63	1005.62	−288.07	467.56	−48.845
600	616.39	1111.35	−302.13	620.03	−53.974
700	678.23	1211.14	−312.63	774.67	−57.803
800	730.82	1305.20	−320.20	930.40	−60.746
900	776.22	1393.98	−324.97	1087.13	−63.091
1000	815.04	1477.83	−327.23	1244.28	−64.991
		1-Eicosene $C_{20}H_{40}$			
300	454.80	932.78	−330.83	208.41	−36.287
400	574.04	1080.23	−358.02	392.50	−51.252
500	681.62	1220.18	−380.20	582.79	−60.879
600	772.74	1352.69	−397.61	776.97	−67.639
700	850.19	1477.79	−410.49	973.91	−72.671
800	916.00	1595.69	−419.66	1172.19	−76.533
900	972.78	1706.95	−425.43	1371.64	−79.605
1000	1021.73	1812.05	−427.98	1571.64	−82.090
		Cyclobutene C_4H_6			
300	67.49	263.93	129.58	175.02	−30.470
400	90.33	286.56	124.68	190.92	−24.931
500	110.33	308.95	120.62	207.99	−21.726
600	126.78	330.54	117.40	225.73	−19.651
700	140.37	351.12	114.89	244.01	−18.208
800	151.71	370.62	112.93	262.59	−17.144
900	161.38	389.07	111.55	281.37	−16.330
1000	169.58	406.52	110.62	300.33	−15.687

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Cyclopentene C_5H_8			
300	75.65	290.16	32.76	111.25	−19.372
400	104.93	315.98	25.02	138.66	−18.106
500	132.30	342.38	18.58	167.82	−17.532
600	155.60	368.65	13.39	198.15	−17.251
700	175.14	394.13	9.33	229.33	−17.111
800	191.54	418.61	6.28	260.91	−17.036
900	205.48	442.00	4.02	292.92	−17.000
1000	217.32	464.30	2.59	325.14	−16.983
		1-Methylcyclopentene C_6H_{10}			
300	101.67	326.98	5.61	102.76	−17.894
400	135.98	361.00	−14.43	140.29	−18.320
500	168.20	394.89	−21.80	179.87	−18.789
600	195.81	427.98	−27.74	220.75	−19.217
700	223.01	460.37	−32.01	262.55	−19.591
800	238.49	491.16	−35.23	304.80	−19.901
900	254.81	520.20	−37.66	347.48	−20.167
1000	269.03	547.81	−39.16	390.41	−20.392
		3-Methylcyclopentene C_6H_{10}			
300	100.83	331.16	8.49	115.60	−20.130
400	136.40	365.14	−0.38	152.72	−19.944
500	169.45	399.20	−7.61	191.88	−20.044
600	197.07	432.63	−13.39	232.30	−20.224
700	220.08	464.76	−17.82	273.68	−20.420
800	239.32	495.43	−21.13	315.52	−20.559
900	255.64	524.59	−23.47	357.73	−20.762
1000	269.87	552.29	−24.89	400.24	−20.904
		4-Methylcyclopentene C_6H_{10}			
300	100.83	329.49	14.60	122.21	−21.281
400	136.40	363.46	5.73	159.49	−20.829
500	169.03	397.48	−1.55	198.82	−20.770
600	196.65	430.83	−7.36	239.45	−20.844
700	219.66	462.92	−11.80	280.96	−20.965
800	238.91	493.54	−15.19	328.00	−21.088
900	255.64	522.67	−17.53	365.43	−21.208
1000	269.45	550.32	−18.95	408.11	−21.316
		Cyclohexene C_6H_{10}			
300	105.77	311.42	−5.52	107.53	−18.723
400	144.93	347.31	−13.68	146.52	−19.134
500	178.99	383.46	−20.04	187.36	−19.571
600	206.90	418.61	−24.81	229.28	−19.959
700	229.79	452.29	−28.28	271.96	−20.292
800	248.91	484.26	−30.63	314.97	−20.564
900	265.01	514.51	−32.01	358.28	−20.793
1000	278.74	543.17	−32.51	401.71	−20.982

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Benzene and Alkylbenzenes			
		Benzene C_6H_6			
300	82.22	269.74	82.80	129.96	−22.623
400	111.88	297.52	77.66	146.48	−19.126
500	137.24	325.31	73.39	164.18	−17.152
600	157.90	352.21	69.91	182.67	−15.901
700	174.68	377.86	67.11	201.71	−15.051
800	188.53	402.12	64.89	221.08	−14.434
900	200.12	425.01	63.18	240.71	−13.970
1000	209.87	446.60	62.01	260.54	−13.608
		Toluene C_7H_8			
300	104.35	321.33	49.87	122.47	−21.320
400	140.08	356.35	43.26	147.70	−19.287
500	171.46	391.08	37.87	174.47	−18.225
600	197.48	424.72	33.56	202.17	−17.599
700	218.95	456.81	30.29	230.58	−17.205
800	236.86	487.23	27.82	259.32	−16.931
900	252.00	516.01	26.11	288.40	−16.736
1000	264.93	543.29	25.15	317.61	−16.589
		Ethylbenzene C_8H_{10}			
300	129.20	361.29	29.62	131.17	−22.841
400	170.54	404.22	21.88	166.27	−21.713
500	206.48	446.27	15.52	203.13	−21.222
600	236.14	486.60	10.38	241.12	−20.992
700	260.58	524.88	6.40	279.95	−20.890
800	280.96	561.07	3.35	319.20	−20.842
900	298.19	595.17	1.13	358.86	−20.827
1000	312.84	627.35	−0.21	398.74	−20.826
		m-Xylene C_8H_{10}			
300	128.28	358.49	17.07	119.45	−20.800
400	167.49	400.87	9.12	154.85	−20.222
500	202.63	442.12	2.38	192.09	−20.068
600	232.25	481.75	−3.14	230.54	−20.069
700	257.02	519.49	−7.49	269.87	−20.138
800	277.86	555.17	−10.88	309.70	−20.220
900	295.52	588.98	−13.35	349.95	−20.310
1000	310.58	620.91	−14.98	390.45	−20.394
		o-Xylene C_8H_{10}			
300	133.97	353.59	18.83	122.72	−21.364
400	171.67	397.40	11.38	158.53	−20.699
500	205.48	439.45	4.98	196.06	−20.481
600	234.22	479.49	−0.29	234.72	−20.435
700	258.40	517.48	−4.48	274.30	−20.467
800	278.82	553.33	−7.74	314.30	−20.521
900	296.23	587.22	−10.17	354.72	−20.587
1000	311.08	619.23	−11.67	395.39	−20.653

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		p-Xylene C_8H_{10}			
300	127.57	353.31	17.78	121.75	−21.199
400	166.10	395.30	9.71	157.69	−20.592
500	201.08	436.22	2.85	195.52	−20.424
600	230.79	475.55	−2.80	234.56	−20.419
700	255.73	513.08	−7.32	274.51	−20.485
800	276.73	548.61	−10.84	315.01	−20.566
900	294.51	582.29	−13.43	355.89	−20.655
1000	309.70	614.13	−15.10	397.06	−20.740
		Propylbenzene C_9H_{12}			
300	153.22	401.62	7.61	138.03	−24.034
400	200.08	452.25	−1.38	182.97	−23.890
500	241.21	501.45	−8.79	229.91	−24.018
600	275.56	548.56	−14.69	278.19	−24.218
700	303.88	593.21	−19.25	327.44	−24.432
800	327.61	635.38	−22.68	377.15	−24.624
900	347.69	675.17	−25.10	427.31	−24.799
1000	364.68	712.70	−26.48	477.69	−24.951
		iso-Propylbenzene C_9H_{12}			
300	152.59	389.53	3.72	137.78	−23.988
400	200.83	440.20	−5.27	183.89	−24.014
500	242.25	489.57	−12.55	232.04	−24.242
600	276.98	536.93	−18.37	281.50	−24.507
700	305.01	581.79	−22.76	331.92	−24.766
800	328.86	624.13	−26.11	382.75	−24.990
900	348.53	664.00	−28.41	434.05	−25.189
1000	365.26	701.61	−29.71	485.55	−25.361
		m-Ethyltoluene C_9H_{12}			
300	153.09	405.14	−2.13	127.24	−22.153
400	198.74	455.55	−11.21	171.80	−22.434
500	239.32	504.38	−18.79	218.45	−22.821
600	273.63	551.16	−24.89	266.48	−23.197
700	301.67	595.47	−29.62	315.47	−23.539
800	325.52	637.35	−33.30	364.97	−23.828
900	346.02	676.93	−35.90	414.93	−24.081
1000	363.17	714.29	−37.45	465.18	−24.296
		o-Ethyltoluene C_9H_{12}			
300	158.74	400.24	1.05	131.84	−22.958
400	202.92	452.08	−7.57	176.86	−23.091
500	242.25	501.70	−14.77	223.80	−23.379
600	275.31	548.86	−20.67	272.04	−23.682
700	303.34	593.46	−25.23	321.25	−23.971
800	326.77	635.55	−28.74	370.95	−24.219
900	346.44	675.17	−31.30	421.08	−24.439
1000	363.59	712.62	−32.80	471.49	−24. 27

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		p-Ethyltoluene C_9H_{12}			
300	152.38	399.86	−3.47	127.49	−22.196
400	197.48	449.99	−12.64	172.59	−22.537
500	238.07	498.52	−20.33	219.83	−22.963
600	271.96	545.01	−26.61	268.40	−23.367
700	300.41	589.15	−31.51	318.03	−23.731
800	324.68	630.86	−35.27	368.19	−24.039
900	344.76	670.32	−37.95	418.82	−24.306
1000	362.33	707.56	−39.62	469.70	−24.533
		1,2,3-Trimethylbenzene C_9H_{12}			
300	154.98	385.81	−9.79	125.39	−21.830
400	196.23	436.14	−18.91	171.88	−22.444
500	234.72	484.13	−26.86	220.50	−23.036
600	267.78	529.95	−33.47	270.58	−23.555
700	296.65	573.42	−38.79	321.75	−24.008
800	320.91	614.67	−42.93	373.51	−24.385
900	341.41	653.67	−45.98	425.76	−24.709
1000	359.41	690.61	−47.95	478.31	−24.984
		1,2,4-Trimethylbenzene C_9H_{12}			
300	154.77	396.73	−14.14	117.74	−20.502
400	196.48	447.06	−23.26	163.18	−21.305
500	235.39	495.18	−31.13	210.71	−22.010
600	268.99	541.12	−37.70	259.66	−22.604
700	297.57	584.80	−42.89	309.70	−23.108
800	321.88	626.14	−46.90	360.28	−23.523
900	342.54	665.30	−48.87	411.41	−23.876
1000	360.24	702.33	−51.76	462.79	−24.174
		1,3,5-Trimethylbenzene C_9H_{12}			
300	151.04	386.27	−16.28	118.74	−20.677
400	194.18	435.68	−25.69	165.27	−21.579
500	233.97	483.42	−33.76	213.97	−22.351
600	268.11	529.15	−40.42	264.09	−22.991
700	297.02	572.71	−45.69	315.35	−23.530
800	321.50	614.00	−49.79	367.15	−23.971
900	342.29	653.12	−52.76	419.49	−24.345
1000	360.12	690.11	−54.64	472.12	−24.659
		Butylbenzene $C_{10}H_{14}$			
300	176.10	440.58	−14.02	145.65	−25.358
400	229.07	498.65	−24.39	200.54	−26.184
500	275.68	554.92	−32.84	257.78	−26.927
600	314.64	608.73	−39.58	316.48	−27.552
700	346.90	659.73	−44.73	376.31	−28.080
800	373.92	707.85	−48.58	436.68	−28.511
900	396.81	753.25	−51.25	497.56	−28.875
1000	416.27	796.09	−52.72	558.65	−29.180

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1,2,3,4-Tetramethylbenzene $C_{10}H_{14}$			
300	190.37	417.73	−42.13	124.43	−21.662
400	237.69	479.07	−51.34	181.42	−23.687
500	280.37	536.81	−59.16	240.50	−25.125
600	316.65	591.20	−65.56	301.04	−26.205
700	347.82	642.41	−70.58	362.59	−27.055
800	374.13	690.65	−74.39	424.68	−27.727
900	396.73	736.05	−77.03	487.27	−28.278
1000	416.18	778.85	−78.49	550.11	−28.733
		1,2,3,5-Tetramethylbenzene $C_{10}H_{14}$			
300	186.48	423.71	−45.02	119.75	−20.845
400	233.30	483.88	−54.64	176.15	−23.004
500	276.27	540.66	−62.89	234.85	−24.533
600	313.01	594.34	−69.71	295.01	−25.682
700	344.72	645.05	−75.06	356.31	−26.586
800	371.50	692.87	−79.12	418.15	−27.301
900	394.43	737.97	−82.01	480.53	−27.887
1000	414.26	780.57	−83.72	543.17	−28.371
		1,2,4,5-Tetramethylbenzene $C_{10}H_{14}$			
300	187.32	419.70	−45.48	120.46	−20.975
400	232.21	479.78	−55.15	177.32	−23.153
500	274.55	536.26	−63.51	236.40	−24.697
600	311.21	589.65	−70.50	297.02	−25.858
700	342.96	640.07	−76.02	358.82	−26.773
800	369.91	687.64	−80.29	421.16	−27.497
900	393.04	732.58	−83.30	484.05	−28.093
1000	413.00	775.09	−85.14	547.27	−28.584
		Pentylbenzene $C_{11}H_{16}$			
300	199.12	480.20	−34.69	154.05	−26.824
400	258.11	545.72	−46.36	218.87	−28.577
500	310.20	609.06	−55.90	286.27	−29.907
600	353.76	669.61	−63.47	355.43	−30.940
700	389.87	726.89	−69.20	425.76	−31.769
800	420.20	780.99	−73.47	496.72	−32.430
900	445.97	832.03	−76.36	568.19	−32.976
1000	467.90	880.19	−77.91	639.98	−33.427
		Hexylbenzene $C_{12}H_{18}$			
300	222.09	519.28	−55.31	162.67	−28.323
400	287.15	592.29	−68.32	237.40	−31.001
500	344.72	622.70	−78.91	315.10	−32.917
600	392.84	729.94	−87.32	394.68	−34.358
700	432.88	793.58	−93.64	475.60	−35.488
800	466.52	853.62	−98.32	557.18	−36.378
900	495.13	910.27	−101.46	639.36	−37.105
1000	519.65	963.74	−103.05	721.82	−37.703

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Hexamethylbenzene $C_{12}H_{18}$			
300	249.91	453.92	−105.90	131.67	−22.923
400	310.37	534.30	−116.36	212.55	−27.753
500	362.54	609.32	−124.93	295.77	−30.898
600	406.39	679.40	−131.80	380.53	−33.127
700	443.38	744.92	−136.90	466.39	−34.802
800	474.93	806.21	−140.62	552.79	−36.092
900	502.04	863.74	−143.01	639.65	−37.123
1000	525.30	917.89	−144.01	726.76	−37.960
		1-Phenylheptane $C_{13}H_{20}$			
300	245.10	558.40	−75.94	171.25	−29.815
400	316.18	638.81	−90.29	255.94	−33.420
500	379.20	716.34	−101.96	343.88	−35.924
600	431.91	790.27	−111.21	433.92	−37.773
700	475.85	860.23	−118.16	525.38	−39.203
800	512.79	926.25	−123.22	617.60	−40.324
900	544.25	988.51	−126.57	710.48	−41.233
1000	571.12	1047.30	−128.28	803.66	−41.976
		1-Phenyloctane $C_{14}H_{22}$			
300	268.07	597.48	−96.57	179.87	−31.314
400	345.22	685.38	−112.26	274.51	−35.844
500	413.71	769.98	−125.02	372.71	−38.934
600	471.03	850.61	−135.06	473.17	−41.191
700	518.86	926.92	−142.59	575.22	−42.922
800	559.07	998.89	−148.07	678.06	−44.272
900	593.42	1066.75	−151.67	781.61	−45.362
1000	622.58	1130.85	−153.43	885.50	−46.252
		1-Phenylnonane $C_{15}H_{24}$			
300	291.08	636.55	−117.24	188.41	−33.806
400	374.26	731.91	−134.22	293.01	−38.262
500	448.19	823.62	−148.07	401.50	−41.941
600	510.11	910.94	−158.91	512.37	−44.605
700	561.83	993.57	−167.07	625.01	−46.638
800	605.38	1071.52	−172.97	738.52	−48.217
900	642.54	1144.99	−176.77	852.74	−49.489
1000	674.46	1214.41	−178.66	967.34	−50.526
		1-Phenyldecane $C_{16}H_{26}$			
300	314.05	675.67	−137.86	196.98	−34.298
400	403.34	778.47	−156.23	311.54	−40.681
500	482.71	877.26	−171.13	430.28	−44.947
600	549.19	971.32	−182.80	551.62	−48.019
700	604.84	1060.23	−191.54	674.84	−50.353
800	651.70	1144.16	−197.86	798.93	−52.162
900	691.70	1223.28	−201.92	923.83	−53.616
1000	725.92	1297.96	−203.84	1049.14	−54.799

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		Dicyclic Hydrocarbons			
		Naphthalene $C_{10}H_{18}$			
300	133.43	336.48	150.83	224.05	−39.007
400	179.20	381.29	144.56	249.45	−32.575
500	218.11	425.60	139.49	276.31	−28.863
600	249.66	468.27	135.39	304.01	−26.465
700	275.18	508.73	132.21	332.42	−24.805
800	296.10	546.85	129.75	361.16	−23.580
900	313.42	582.75	127.95	390.20	−22.646
1000	327.94	616.55	126.90	419.45	−21.908
		1-Methylnaphthalene $C_{11}H_{10}$			
300	160.54	378.44	116.69	218.28	−38.005
400	212.30	431.91	109.54	253.30	−33.077
500	256.27	484.17	103.76	289.95	−30.289
600	292.00	534.13	99.20	327.57	−28.517
700	321.16	581.41	95.73	365.97	−27.309
800	345.10	625.88	93.14	404.72	−26.425
900	364.80	667.72	91.34	443.80	−25.757
1000	381.61	707.05	90.42	483.08	−25.232
		2-Methylnaphthalene $C_{11}H_{10}$			
300	160.75	381.04	115.94	216.77	−36.738
400	211.29	434.38	108.74	251.54	−32.844
500	254.68	486.35	102.84	287.94	−30.078
600	289.99	535.97	98.07	325.35	−28.324
700	319.16	582.96	94.43	363.59	−27.131
800	343.21	627.18	91.63	402.21	−26.260
900	363.21	668.77	89.66	441.16	−25.603
1000	380.16	707.97	88.58	480.32	−25.088
		1-Ethylnaphthalene $C_{12}H_{12}$			
300	185.35	419.32	96.48	226.73	−39.478
400	243.72	480.83	88.16	271.50	−35.455
500	293.13	540.70	81.59	318.15	−33.235
600	333.26	597.81	76.40	365.89	−31.854
700	365.97	651.70	72.55	414.55	−30.932
800	392.92	702.41	69.71	463.55	−30.265
900	415.22	749.98	67.82	512.92	−29.767
1000	434.26	794.75	66.94	562.46	−29.378
		2-Ethylnaphthalene $C_{12}H_{12}$			
300	185.56	421.91	95.73	225.22	−39.211
400	242.71	483.34	87.36	269.74	−35.221
500	291.54	542.87	80.67	316.14	−33.024
600	331.25	599.65	75.31	363.67	−31.660
700	363.67	653.25	71.25	412.17	−30.754
800	391.04	703.67	68.20	460.99	−30.099
900	413.63	751.07	66.15	510.24	−29.613
1000	432.79	795.67	65.10	559.69	−29.235

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1,2-Dimethylnaphthalene $C_{12}H_{12}$			
300	186.02	407.98	83.39	217.07	−37.790
400	243.84	469.61	75.10	262.96	−34.336
500	293.13	529.49	68.53	310.70	−32.457
600	333.21	586.60	63.35	359.57	−31.303
700	366.14	640.49	59.50	409.32	−30.544
800	393.13	691.20	56.69	459.45	−29.998
900	415.26	738.81	54.81	509.95	−29.595
1000	434.42	783.58	53.93	560.61	−29.282
		1,3-Dimethylnaphthalene $C_{12}H_{12}$			
300	186.23	410.62	81.63	214.51	−37.347
400	242.84	472.12	73.30	260.16	−34.969
500	291.54	531.70	66.61	307.65	−32.139
600	331.21	588.48	61.21	356.35	−31.020
700	364.13	642.08	57.20	405.93	−30.288
800	391.25	692.54	54.18	455.89	−29.765
900	413.67	739.94	52.13	506.26	−29.381
1000	432.96	784.54	51.09	556.81	−29.084
		1,4-Dimethylnaphthalene $C_{12}H_{12}$			
300	186.02	402.25	82.34	217.74	−37.907
400	243.84	463.88	74.06	264.18	−34.499
500	293.13	523.75	67.49	312.50	−32.647
600	333.21	580.86	62.30	362.00	−31.512
700	366.14	634.75	58.45	412.29	−30.765
800	393.13	685.46	55.68	463.00	−30.229
900	415.26	733.08	53.76	514.05	−29.834
1000	434.42	777.85	52.89	565.30	−29.527
		Azulene $C_{10}H_8$			
300	129.41	338.69	279.74	352.33	−61.343
400	176.36	382.50	273.17	377.56	−49.305
500	216.27	426.31	267.86	404.34	−42.238
600	248.19	468.65	263.59	432.00	−37.606
700	274.30	508.90	260.33	460.37	−34.352
800	295.35	546.97	257.78	489.11	−31.933
900	312.75	582.79	255.89	518.15	−30.070
1000	327.36	616.51	254.76	547.35	−28.590
		cis-Decahydronaphthalene $C_{10}H_{18}$			
300	167.95	377.77	−169.28	87.36	−15.213
400	236.98	436.73	−185.48	175.52	−22.918
500	299.74	496.52	−198.15	267.27	−27.922
600	352.04	555.93	−207.69	361.29	−31.450
700	396.27	613.63	−214.35	456.73	−34.079
800	432.46	668.94	−218.70	552.83	−36.094
900	462.96	721.70	−221.04	649.48	−34.692
1000	489.15	771.86	−221.54	746.30	−38.980

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		trans-Decahydronaphthalene $C_{10}H_{18}$			
300	168.87	375.60	−182.63	74.98	−13.055
400	237.57	433.80	−198.70	163.43	−21.340
500	297.65	493.38	−211.54	255.48	−26.690
600	352.29	552.62	−221.12	349.82	−30.452
700	396.52	610.36	−221.74	445.55	−33.247
800	432.63	665.72	−232.09	542.00	−35.388
900	463.04	718.48	−234.43	638.98	−37.083
1000	489.24	768.64	−234.93	736.13	−38.449
		Diphenyl $C_{12}H_{10}$			
300	163.39	393.71	181.92	280.66	−48.864
400	221.04	448.82	174.32	314.80	−41.107
500	269.37	503.50	168.32	350.66	−36.631
600	307.69	556.14	163.59	387.52	−33.736
700	338.61	605.97	160.04	425.55	−31.728
800	363.67	652.87	157.32	463.21	−30.244
900	384.34	696.93	155.39	501.58	−29.110
1000	401.66	738.35	154.35	540.15	−28.214
		Alkynes			
		Acetylene (ethyne) C_2H_2			
300	44.06	201.12	226.73	209.07	−36.401
400	50.08	214.68	226.48	203.22	−26.538
500	54.27	226.31	226.10	197.44	−20.627
600	57.45	236.48	225.60	191.75	−16.693
700	60.12	245.56	225.02	186.19	−13.892
800	62.47	253.76	224.35	180.67	−11.795
900	64.64	261.21	223.63	175.23	−10.170
1000	66.61	268.15	222.97	169.91	−8.875
		Propyne C_3H_4			
300	60.88	248.49	185.39	194.47	−33.859
400	72.51	267.65	183.18	197.86	−25.836
500	82.59	284.93	181.08	201.75	−21.077
600	91.21	300.79	179.20	206.06	−17.939
700	98.66	315.43	177.49	210.71	−15.722
800	105.19	329.03	176.02	215.52	−14.072
900	110.92	341.75	174.77	220.54	−12.800
1000	115.94	353.72	173.76	225.73	−11.789
		1-Butyne C_4H_6			
300	81.76	291.37	165.10	202.30	−35.220
400	99.87	317.40	161.38	215.27	−28.111
500	115.60	341.41	158.07	229.16	−23.937
600	129.00	363.72	155.18	243.63	−21.208
700	140.46	384.47	152.80	258.57	−19.294
800	150.41	403.92	150.79	273.80	−17.876
900	159.08	422.12	149.20	289.28	−16.789
1000	166.69	439.28	148.03	304.93	−15.928

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		2-Butyne C_4H_6			
300	78.24	283.80	146.23	185.69	−32.328
400	94.64	308.57	142.05	199.49	−26.049
500	110.29	331.41	138.20	214.30	−22.386
600	124.18	352.75	134.81	229.83	−20.007
700	136.36	372.84	131.96	245.89	−18.349
800	147.03	391.75	129.58	262.34	−17.127
900	156.31	409.61	127.70	279.03	−16.195
1000	164.39	426.52	126.27	295.98	−15.459
		Dienes			
		Propadiene (allene) C_3H_4			
300	58.99	243.93	192.13	202.38	−35.24
400	72.01	263.13	189.68	206.24	−26.93
500	82.93	280.41	187.65	210.62	−22.00
600	92.05	296.35	185.81	215.35	−18.75
700	99.75	311.16	184.26	220.41	−16.45
800	106.36	324.93	182.88	225.68	−14.73
900	112.13	337.77	181.75	231.08	−13.41
1000	117.15	349.87	180.87	236.65	−12.36
1100	121.50	361.20	180.16	242.09	−11.50
1500	134.10	401.00	178.57	264.96	−9.23
		1,2-Butadiene C_4H_6			
300	80.45	293.51	162.13	198.66	−34.59
400	98.49	319.20	158.23	211.46	−27.61
500	114.60	342.92	154.81	225.18	−23.52
600	128.53	365.10	151.88	239.49	−20.82
700	140.33	385.81	149.45	254.30	−18.97
800	150.67	405.22	147.44	269.41	−17.59
900	159.66	423.50	145.90	284.76	−16.53
1000	167.44	440.74	144.81	300.29	−15.68
1100	174.10	457.00	144.06	315.75	−15.00
1500	193.30	514.10	143.13	378.36	−13.18
		1,3-Butadiene C_4H_6			
300	79.96	279.24	110.08	150.92	−26.27
400	101.63	305.31	106.36	165.10	−21.56
500	119.33	329.95	103.34	180.16	−18.82
600	133.22	353.00	100.88	195.73	−17.04
700	144.56	374.38	98.87	211.71	−15.80
800	154.14	394.34	97.28	227.94	−14.88
900	162.38	413.00	96.02	244.35	−14.18
1000	169.54	430.49	95.14	260.91	−13.63
1100	175.80	446.90	94.64	277.44	−13.18
1500	193.30	504.30	94.01	343.95	−11.98

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1,2-Pentadiene C_5H_8			
300	105.86	334.13	145.48	210.79	−36.70
400	131.38	368.19	140.62	233.34	−30.47
500	152.72	399.86	136.48	257.02	−26.85
600	170.71	429.32	133.05	281.42	−24.50
700	186.19	456.85	130.33	306.39	−22.86
800	199.58	482.58	128.20	331.67	−21.66
900	210.87	506.77	126.65	357.23	−20.73
1000	220.92	529.53	125.65	382.96	−20.00
1100	229.70	551.00	125.35	408.58	−19.41
1500	254.00	626.30	125.05	511.33	−17.81
		cis-1,3-Pentadiene C_5H_8			
300	94.98	324.89	78.11	146.19	−25.45
400	123.43	356.18	72.30	169.83	−22.18
500	147.70	386.43	67.53	194.77	−20.35
600	166.94	415.09	63.68	220.58	−19.20
700	183.26	442.08	60.58	247.02	−18.43
800	196.65	467.48	58.16	273.76	−17.87
900	208.36	491.33	56.36	300.87	−17.46
1000	218.40	513.80	55.10	328.11	−17.14
1100	227.20	535.10	54.56	355.32	−16.88
1500	252.30	609.60	54.10	464.81	−16.19
		trans-1,3-Pentadiene C_5H_8			
300	104.18	320.33	77.70	147.15	−25.62
400	130.54	354.01	72.72	171.13	−22.34
500	153.13	385.64	68.57	196.19	−20.50
600	171.13	415.18	65.19	222.04	−19.33
700	186.61	442.75	62.51	248.45	−18.54
800	199.58	468.52	60.38	275.10	−17.96
900	210.46	492.71	58.79	302.07	−17.53
1000	220.08	515.38	57.74	329.20	−17.19
1100	228.90	536.80	57.28	356.17	−16.92
1500	253.10	611.70	57.07	464.53	−16.18
		1,4-Pentadiene C_5H_8			
300	105.44	334.16	105.31	170.62	−29.71
400	130.96	368.07	100.42	193.17	−25.23
500	152.72	399.70	96.27	216.86	−22.66
600	170.71	429.15	92.84	241.29	−21.01
700	185.77	456.64	90.08	266.31	−19.87
800	199.16	482.33	87.91	291.58	−19.04
900	210.46	506.47	86.32	317.19	−18.41
1000	220.50	529.15	85.27	342.92	−17.91
1100	228.90	550.60	84.81	368.59	−17.51
1500	253.60	625.50	85.10	471.99	−16.44

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		2,3-Pentadiene C_5H_8			
300	101.67	325.35	138.36	206.31	−35.92
400	125.10	357.82	128.78	229.83	−30.01
500	146.44	388.11	128.20	254.60	−26.60
600	164.85	416.48	124.18	280.24	−24.40
700	180.75	443.09	120.86	306.56	−22.88
800	194.97	468.19	118.24	333.26	−21.76
900	207.11	491.87	116.23	360.28	−20.91
1000	217.57	514.26	114.93	387.48	−20.24
1100	226.80	535.60	114.22	414.47	−19.69
1500	252.30	610.00	114.14	524.24	−18.26
		3-Methyl-1,2-butadiene C_5H_8			
300	105.86	320.33	129.58	199.03	−34.65
400	129.70	354.13	124.60	222.97	−29.18
500	150.62	385.35	120.29	248.07	−25.92
600	168.62	414.47	116.65	273.97	−23.85
700	184.10	441.62	113.72	300.45	−22.42
800	197.48	467.10	111.38	327.27	−21.37
900	209.20	491.08	109.62	354.38	−20.57
1000	219.24	513.63	108.49	381.66	−19.94
1100	228.00	534.70	107.61	408.79	−19.42
1500	253.10	609.60	107.70	518.50	−18.06
		3-Methyl-1,3-butadiene (isoprene) C_5H_8			
300	105.44	316.31	75.60	146.27	−25.47
400	133.05	350.54	70.79	170.58	−22.28
500	155.23	382.71	66.90	196.02	−20.48
600	173.22	412.63	63.72	222.13	−19.34
700	188.28	440.49	61.21	248.74	−18.56
800	200.83	466.47	59.24	275.64	−18.00
900	211.71	490.78	57.82	302.80	−17.57
1000	221.33	513.58	56.90	330.12	−17.24
1100	229.70	535.10	56.48	357.22	−16.97
1500	253.60	610.00	56.61	466.82	−16.26
		Styrenes, Ethynylbenzene			
		Styrene C_8H_8			
300	122.80	345.89	147.23	214.18	−37.29
400	160.33	386.48	141.55	237.44	−31.00
500	192.21	425.81	136.90	261.96	−25.36
600	218.15	463.21	133.09	287.32	−25.01
700	239.37	498.48	130.08	313.30	−23.38
800	256.90	531.62	127.70	339.57	−22.17
900	271.67	562.75	125.94	366.18	−21.25
1000	284.18	592.04	124.81	392.96	−20.53
1100	294.90	619.70	124.22	419.53	−19.93
1500	324.60	715.90	124.18	527.12	−18.36

Table A.21 (*continued*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		1-Methylstyrene C_9H_{10}			
300	146.02	384.59	112.80	209.12	−36.41
400	187.44	432.37	105.73	242.34	−31.65
500	223.84	478.23	99.75	277.19	−28.96
600	253.97	521.79	94.77	313.13	−27.26
700	279.49	562.92	90.88	349.91	−26.11
800	300.41	601.62	87.82	387.06	−25.27
900	318.40	638.10	85.52	424.63	−24.64
1000	333.88	672.45	84.14	462.46	−24.16
1100	346.90	705.00	83.39	499.04	−23.75
1500	383.30	818.00	83.30	652.00	−22.71
		cis-2-Methylstyrene C_9H_{10}			
300	146.02	384.59	121.17	217.48	−37.86
400	187.44	432.37	114.10	250.71	−32.74
500	223.84	478.23	108.11	285.56	−29.83
600	253.97	521.79	103.14	321.50	−27.99
700	279.49	562.92	99.24	358.28	−26.73
800	300.41	601.62	96.19	395.43	−25.82
900	318.40	638.10	93.89	433.00	−25.13
1000	333.88	672.45	92.51	470.74	−24.59
1100	346.90	705.00	91.76	508.36	−24.15
1500	383.30	818.00	91.76	660.33	−23.00
		trans-2-Methylstyrene C_9H_{10}			
300	146.86	381.25	116.98	214.30	−37.31
400	189.12	429.40	110.04	247.86	−32.36
500	225.94	475.68	104.22	283.00	−29.56
600	256.06	519.61	99.50	319.16	−27.78
700	281.16	561.03	95.77	356.14	−26.57
800	302.08	599.99	92.88	393.46	−25.69
900	319.66	636.60	90.75	431.20	−25.03
1000	334.72	671.07	89.45	469.15	−24.50
1100	347.70	703.70	88.99	506.88	−24.08
1500	383.70	817.10	89.33	659.18	−22.96
		o-Methylstyrene C_9H_{10}			
300	146.02	384.59	118.24	214.56	−37.35
400	187.44	432.37	111.17	247.78	−32.36
500	223.84	478.23	105.19	282.63	−29.53
600	253.97	521.79	100.21	318.57	−27.73
700	279.49	562.92	96.32	355.35	−26.52
800	300.41	601.62	93.26	392.50	−25.63
900	318.40	638.10	90.96	430.07	−24.96
1000	333.88	672.45	89.58	467.90	−24.44
1100	346.90	705.00	88.83	505.41	−24.01
1500	383.30	818.00	88.83	657.46	−22.90

Table A.21 (*concluded*)

T, K	C_p°, J/(mol·K)	S°, J/(mol·K)	ΔH_f°, kJ/mol	ΔG_f°, kJ/mol	$\log K_{p,f}^\circ$
		m-Methylstyrene C_9H_{10}			
300	146.02	390.45	115.31	209.87	−36.54
400	187.44	438.23	108.24	242.50	−36.67
500	223.84	484.09	102.26	276.77	−28.92
600	253.97	527.64	97.28	312.13	−27.17
700	279.49	568.77	93.39	348.32	−25.99
800	300.41	607.47	90.33	384.89	−25.13
900	318.40	643.96	88.03	421.87	−24.48
1000	333.88	678.31	86.65	459.53	−23.98
1100	346.90	710.90	85.90	495.94	−23.56
1500	383.30	823.00	85.90	645.69	−22.49
		p-Methylstyrene C_9H_{10}			
300	146.02	384.59	114.47	210.79	−36.70
400	187.44	432.37	107.40	244.01	−31.86
500	223.84	478.23	101.42	278.86	−29.13
600	253.97	521.79	96.44	314.80	−27.41
700	279.49	562.92	92.55	351.58	−26.23
800	300.41	601.62	89.50	388.74	−25.38
900	318.40	638.10	87.19	426.31	−24.74
1000	333.88	672.45	85.81	464.13	−24.24
1100	346.90	705.00	85.06	501.62	−23.83
1500	383.30	818.00	85.06	653.44	−22.76
		Ethynylbenzene (phenylacetylene) C_8H_6			
300	115.60	322.42	327.19	361.96	−63.019
400	150.41	360.58	323.55	374.13	−48.856
500	178.53	397.27	320.66	387.15	−40.442
600	200.87	431.87	318.19	400.62	−34.877
700	218.78	464.21	316.27	414.59	−30.934
800	233.43	494.42	314.64	428.69	−27.990
900	245.64	522.62	313.34	443.04	−25.712
1000	255.94	549.07	312.54	457.52	−23.897

Table A.22. **Thermodynamic Functions of Oxygen-Containing Hydrocarbon Derivatives [in the State of an Ideal Gas; C_p° and S° are in J/(mol·K), ΔH_f° is in kJ/mol, and $K_{p,f}^\circ$ is a dimensionless quantity]**

Substance		Temperature, K			
		300	500	700	1000
		Alcohols			
Methanol CH_4O	C_p°	44.02	59.50	73.72	89.45
	S°	239.99	266.02	288.36	317.48
	ΔH_f°	−201.25	−207.94	−212.88	−217.28
	$\log K_{p,f}^\circ$	28.252	14.032	7.756	2.941

Table A.22 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Ethanol C_2H_6O	C_p°	65.73	95.27	117.95	141.54
	S°	283.01	323.67	359.53	405.85
	ΔH_f°	−234.89	−243.97	−250.04	−254.93
	$\log K_{p,f}^\circ$	29.231	12.590	5.222	−0.433
1-Propanol (*n*-propyl alcohol) C_3H_8O	C_p°	87.49	127.65	159.12	192.17
	S°	325.35	379.70	427.90	490.62
	ΔH_f°	−257.65	−269.45	−277.36	−283.38
	$\log K_{p,f}^\circ$	28.273	9.963	1.807	−4.474
2-Propanol (*iso*-propyl alcohol) C_3H_8O	C_p°	89.16	133.43	164.05	195.89
	S°	310.49	366.69	416.64	480.91
	ΔH_f°	−272.71	−283.76	−290.62	−295.31
	$\log K_{p,f}^\circ$	30.118	10.776	2.208	4.355
1-Butanol $C_4H_{10}O$	C_p°	110.50	162.17	202.13	243.76
	S°	363.88	432.75	493.96	573.58
	ΔH_f°	−274.60	−288.82	−298.11	−304.85
	$\log K_{p,f}^\circ$	26.102	6.537	−2.217	−8.972
2-Butanol $C_4H_{10}O$	C_p°	113.80	166.10	205.10	245.27
	S°	359.74	430.49	492.92	573.33
	ΔH_f°	−292.46	−305.93	−314.55	−320.62
	$\log K_{p,f}^\circ$	28.997	8.208	−1.047	−8.162
2-Methyl-2-propanol $C_4H_{10}O$	C_p°	113.93	168.49	207.69	247.53
	S°	326.98	398.53	461.83	543.13
	ΔH_f°	−325.98	−339.11	−347.19	−352.54
	$\log K_{p,f}^\circ$	33.120	10.005	−0.233	−8.072

Table A.22 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
1-Pentanol $C_5H_{12}O$	C_p°	133.51	196.69	245.14	295.35
	S°	403.38	486.81	561.07	657.56
	ΔH_f°	−302.59	−319.20	−329.91	−337.36
	$\log K_{p,f}^\circ$	25.907	4.318	−5.364	−12.841
2-Methyl-2-butanol $C_5H_{12}O$	C_p°	132.34	199.49	249.32	298.74
	S°	367.69	451.50	527.06	624.84
	ΔH_f°	−329.28	−345.68	−355.64	−362.04
	$\log K_{p,f}^\circ$	28.691	5.243	−5.221	−13.262
1-Hexanol $C_6H_{14}O$	C_p°	156.52	231.21	288.15	346.94
	S°	442.50	540.45	627.73	741.15
	ΔH_f°	−319.82	−338.86	−351.00	−359.20
	$\log K_{p,f}^\circ$	23.825	0.957	−9.332	−17.291
1-Octanol $C_8H_{18}O$	C_p°	202.55	300.24	374.18	450.11
	S°	520.66	647.73	761.07	908.26
	ΔH_f°	−357.36	−381.16	−396.14	−405.76
	$\log K_{p,f}^\circ$	20.178	−5.453	−17.047	−26.037
1-Decanol $C_{10}H_{22}O$	C_p°	248.57	369.28	460.20	553.29
	S°	598.86	755.00	894.41	1075.41
	ΔH_f°	−403.59	−432.21	−450.03	−461.12
	$\log K_{p,f}^\circ$	18.054	−10.950	−24.110	−34.326
1-Dodecanol $C_{12}H_{26}O$	C_p°	294.60	438.32	546.22	656.47
	S°	677.05	862.28	1027.76	1242.56
	ΔH_f°	−443.21	−476.64	−497.35	−509.82
	$\log K_{p,f}^\circ$	14.779	−17.137	−31.666	−42.960
1-Hexadecanol $C_{16}H_{34}O$	C_p°	386.39	576.22	718.10	863.16
	S°	832.07	1075.41	1293.07	1575.40
	ΔH_f°	−525.76	−568.77	−595.17	−610.57
	$\log K_{p,f}^\circ$	8.726	−29.241	−46.604	−60.130

Table A.22 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
1-Eicosanol $C_{20}H_{42}O$	C_p°	478.31	714.25	890.10	1069.85
	S°	988.47	1289.97	1559.75	1909.66
	ΔH_f°	−608.35	−660.99	−693.04	−711.36
	$\log K_{p,f}^\circ$	2.751	−41.271	−61.470	−77.226
Ethyleneglycol C_2H_6O	C_p°	97.40	125.94	146.44	166.86
	S°	324.18	381.08	426.89	482.54
	ΔH_f°	−389.40	−395.10	−398.48	−400.66
	$\log K_{p,f}^\circ$	52.917	25.617	13.775	4.827
Cyclohexanol $C_6H_{12}O$	C_p°	127.99	212.97	277.52	339.45
	S°	328.49	414.34	496.89	607.27
	ΔH_f°	−294.76	−312.59	−321.71	−323.47
	$\log K_{p,f}^\circ$	20.338	−0.762	−10.232	−17.474
2-Propen-1-ol (allyl alcohol) C_3H_6O	C_p°	76.36	112.09	137.70	163.43
	S°	308.07	355.85	397.66	451.66
	ΔH_f°	−132.09	−140.67	−146.44	−151.08
	$\log K_{p,f}^\circ$	12.340	2.871	−1.410	−4.742
Aldehydes					
Formaldehyde (methanal) CH_2O	C_p°	35.44	43.76	52.26	61.97
	S°	219.03	238.95	255.10	275.47
	ΔH_f°	−115.94	−119.24	−122.05	−124.93
	$\log K_{p,f}^\circ$	19.133	10.961	7.363	4.599
Acetaldehyde (ethanal) C_2H_4O	C_p°	54.70	76.44	94.14	112.80
	S°	264.60	297.73	326.39	363.34
	ΔH_f°	−166.44	−172.67	−177.19	−181.04
	$\log K_{p,f}^\circ$	23.174	11.393	6.176	2.165
Propionaldehyde (propanal) C_3H_6O	C_p°	78.95	112.51	138.20	164.31
	S°	305.22	353.22	395.89	449.95
	ΔH_f°	−192.13	−200.46	−206.10	−210.54
	$\log K_{p,f}^\circ$	22.644	9.005	2.941	−1.725

Table A.22 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Butyraldehyde (butanal) C_4H_8O	C_p°	102.97	147.28	181.59	216.13
	S°	345.60	408.94	464.26	535.30
	ΔH_f°	−205.14	−215.73	−222.76	−227.82
	$\log K_{p,f}^\circ$	19.885	5.269	−1.271	−6.319
Valeraldehyde (pentanal) $C_5H_{10}O$	C_p°	125.85	181.59	224.68	267.78
	S°	383.76	461.58	529.95	617.93
	ΔH_f°	−227.99	−241.00	−249.41	−255.18
	$\log K_{p,f}^\circ$	18.724	2.441	−4.874	−10.528
Decanal $C_{10}H_{20}O$	C_p°	240.79	354.38	439.32	525.93
	S°	580.07	730.61	864.12	1036.59
	ΔH_f°	−331.21	−356.23	−371.79	−381.16
	$\log K_{p,f}^\circ$	11.300	−12.551	−23.410	−31.854
		Ketones			
Acetone (2-Propanone) C_3H_6O	C_p°	75.19	108.32	135.31	163.80
	S°	295.43	341.71	382.63	436.01
	ΔH_f°	−217.65	−226.86	−233.22	−238.20
	$\log K_{p,f}^\circ$	26.577	11.135	4.273	−1.007
2-Butanone C_4H_8O	C_p°	103.26	145.44	179.20	214.76
	S°	338.78	401.54	456.10	526.43
	ΔH_f°	−238.49	−249.32	−256.77	−262.42
	$\log K_{p,f}^\circ$	25.335	8.392	0.843	−4.973
2-Pentanone $C_5H_{10}O$	C_p°	121.59	179.08	222.00	266.14
	S°	376.94	453.17	520.62	607.81
	ΔH_f°	−258.82	−272.46	−281.42	−287.86
	$\log K_{p,f}^\circ$	23.738	5.288	−2.973	−9.351
Cyclohexanone $C_6H_{12}O$	C_p°	110.42	188.28	248.95	305.43
	S°	322.88	397.94	471.54	570.91
	ΔH_f°	−230.33	−246.60	−255.18	−257.27
	$\log K_{p,f}^\circ$	15.652	−0.907	−8.398	−14.151
Ketene C_2H_2O	C_p°	51.92	65.61	74.90	84.73
	S°	242.13	272.09	295.73	324.22
	ΔH_f°	−61.09	−62.84	−64.52	−66.65
	$\log K_{p,f}^\circ$	10.495	6.188	4.290	2.824

Table A.22 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Acids, Acid Anhydrides, Esters					
Formic acid CH_2O_2	C_p°	45.35	61.17	72.47	83.47
	S°	249.03	276.10	298.53	326.35
	ΔH_f°	−378.65	−382.17	−384.38	−386.06
	$\log K_{p,f}^\circ$	61.084	34.602	23.164	14.539
Acetic acid $C_2H_4O_2$	C_p°	66.82	94.56	114.43	133.85
	S°	282.92	323.88	359.03	403.30
	ΔH_f°	−434.93	−441.08	−444.93	−447.13
	$\log K_{p,f}^\circ$	65.520	35.036	21.817	11.823
Acrylic acid $C_3H_4O_2$	C_p°	78.12	111.13	133.89	155.31
	S°	315.52	363.59	404.80	456.39
	ΔH_f°	−285.77	−341.96	−345.56	−348.28
	$\log K_{p,f}^\circ$	49.751	26.149	15.892	8.124
Benzoic acid $C_7H_6O_2$	C_p°	104.01	170.54	217.82	260.66
	S°	369.66	438.78	504.21	589.82
	ΔH_f°	−290.33	−302.75	−311.08	−318.28
	$\log K_{p,f}^\circ$	36.547	15.938	6.782	−0.262
Methyl formate $C_2H_4O_2$	C_p°	66.94	94.56	114.64	133.89
	S°	301.67	342.63	377.82	422.12
	ΔH_f°	−349.87	−356.02	−359.82	−362.63
	$\log K_{p,f}^\circ$	51.689	27.130	16.449	8.360
Ethyl acetate $C_4H_8O_2$	C_p°	113.97	161.92	199.53	234.51
	S°	363.46	432.79	493.67	571.28
	ΔH_f°	−443.04	−454.30	−461.20	−465.85
	$\log K_{p,f}^\circ$	56.882	25.675	12.015	1.635
Phenols					
Phenol C_6H_6O	C_p°	104.18	161.67	198.49	232.17
	S°	316.27	383.88	444.59	521.54
	ΔH_f°	−96.44	−104.18	−108.83	−112.13
	$\log K_{p,f}^\circ$	5.661	−1.306	−4.482	−6.958

Table A.22 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
m-Cresol C_7H_8O	C_p°	125.14	193.30	239.28	286.60
	S°	357.56	438.40	511.24	604.80
	ΔH_f°	−132.47	−143.13	−149.70	−153.93
	$\log K_{p,f}^\circ$	6.958	−2.607	−6.974	−10.379
o-Cresol C_7H_8O	C_p°	131.00	196.27	240.83	287.94
	S°	358.44	441.50	515.09	609.15
	ΔH_f°	−128.74	−138.53	−144.68	−148.53
	$\log K_{p,f}^\circ$	6.353	−2.923	−7.147	−10.436
p-Cresol C_7H_8O	C_p°	125.14	192.76	238.61	286.19
	S°	348.44	429.11	501.75	595.13
	ΔH_f°	−125.52	−136.23	−142.93	−147.36
	$\log K_{p,f}^\circ$	5.272	−3.810	−7.973	−11.229
Ethers					
Dimethyl ether C_2H_6O	C_p°	66.07	93.01	116.15	141.38
	S°	267.48	307.57	342.71	388.65
	ΔH_f°	−184.14	−193.47	−199.95	−205.14
	$\log K_{p,f}^\circ$	19.583	6.473	0.606	−3.931
Ethylmethyl ether C_3H_8O	C_p°	90.08	127.74	159.45	193.22
	S°	311.21	366.10	414.38	477.35
	ΔH_f°	−216.56	−228.15	−236.02	−241.84
	$\log K_{p,f}^\circ$	20.379	4.939	−1.983	−7.337
Diethyl ether $C_4H_{10}O$	C_p°	112.97	162.21	202.46	244.81
	S°	343.38	412.79	474.09	553.96
	ΔH_f°	−252.38	−266.40	−275.68	−282.17
	$\log K_{p,f}^\circ$	21.163	3.154	−4.930	−11.181
Dipropyl ether $C_6H_{14}O$	C_p°	158.95	231.21	288.44	347.98
	S°	423.50	521.99	609.36	723.00
	ΔH_f°	−293.09	−311.92	−324.05	−332.00
	$\log K_{p,f}^\circ$	18.178	−2.819	−12.304	−19.658

Table A.22 (*concluded*)

Substance		Temperature, K			
		300	500	700	1000
Diisopropyl ether $C_6H_{14}O$	C_p°	158.95	231.21	288.44	347.98
	S°	391.25	489.74	577.10	690.74
	ΔH_f°	−319.03	−337.86	−349.99	−357.94
	$\log K_{p,f}^\circ$	21.010	−1.794	−12.054	−19.988
Ethylene oxide C_2H_4O	C_p°	48.53	75.44	95.31	114.93
	S°	242.76	274.01	302.75	340.33
	ΔH_f°	−51.72	−59.62	−64.10	−67.45
	$\log K_{p,f}^\circ$	2.236	−1.652	−3.496	−4.970
Propylene oxide C_3H_6O	C_p°	72.72	110.71	138.53	166.48
	S°	287.19	333.59	375.51	429.99
	ΔH_f°	−92.88	−101.96	−107.73	−111.80
	$\log K_{p,f}^\circ$	4.418	−2.335	−5.462	−7.924
Furan C_4H_4O	C_p°	65.90	107.65	134.43	158.53
	S°	267.61	311.71	352.50	404.89
	ΔH_f°	−34.77	−41.30	−45.23	−48.24
	$\log K_{p,f}^\circ$	−0.190	−2.821	−4.110	−5.157
Dioxan (diethylene ether) $C_4H_8O_2$	C_p°	94.56	156.86	201.88	272.88
	S°	300.37	363.59	424.05	503.59
	ΔH_f°	−315.22	−328.74	−335.85	−338.82
	$\log K_{p,f}^\circ$	31.331	8.944	−0.975	−8.537

Table A.23. **Thermodynamic Functions of Halogen-Containing, Nitrogen-Containing, and Sulphur-Containing Hydrocarbon Derivatives (in the state of an ideal gas; C_p° and S° are in J/(mol·K), ΔH_f° is in kJ/mol, and $K_{p,f}^\circ$ is a dimensionless quantity)**

Substance		Temperature, K			
		300	500	700	1000
Halogen-Containing Compounds					
Fluoromethane CH_3F	C_p°	37.61	51.30	63.72	77.15
	S°	223.05	245.39	264.72	289.87
	ΔH_f°	−233.92	−239.49	−243.59	−247.32
	$\log K_{p,f}^\circ$	36.536	20.077	12.870	7.378

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Difluoromethane CH_2F_2	C_p°	43.01	58.99	71.46	83.60
	S°	246.90	272.67	294.60	322.34
	ΔH_f°	−452.92	−457.48	−460.62	−463.21
	$\log K_{p,f}^\circ$	74.024	42.341	28.641	18.304
Trifluoromethane CHF_3	C_p°	51.21	69.25	81.00	90.96
	S°	259.91	290.91	316.23	346.90
	ΔH_f°	−697.56	−700.44	−702.16	−703.29
	$\log K_{p,f}^\circ$	115.412	66.740	45.808	30.083
Tetrafluoromethane CF_4	C_p°	61.63	81.30	92.01	100.04
	S°	261.92	298.44	327.69	362.04
	ΔH_f°	−933.03	−934.12	−934.12	−933.24
	$\log K_{p,f}^\circ$	154.634	89.613	61.729	40.835
Fluoroethane C_2H_5F	C_p°	59.29	86.69	107.82	129.62
	S°	265.31	302.21	334.89	377.31
	ΔH_f°	−261.58	−269.53	−274.85	−278.95
	$\log K_{p,f}^\circ$	36.427	17.964	9.843	3.645
1,1-Difluoroethane $C_2H_4F_2$	C_p°	68.24	96.52	116.57	136.23
	S°	282.96	324.76	360.62	405.76
	ΔH_f°	−987.59	−1000.31	−1008.43	−1014.12
	$\log K_{p,f}^\circ$	75.891	41.303	26.316	14.999
Hexafluoroethane C_2F_6	C_p°	106.82	139.16	155.44	166.44
	S°	332.75	395.72	445.43	503.04
	ΔH_f°	−1343.06	−1342.69	−1340.85	−1337.46
	$\log K_{p,f}^\circ$	218.825	125.288	85.234	55.265
1,1-Difluoroethylene $C_2H_2F_2$	C_p°	59.33	81.63	95.27	107.70
	S°	265.56	301.54	331.33	367.61
	ΔH_f°	−345.22	−348.11	−349.91	−351.37
	$\log K_{p,f}^\circ$	55.947	31.812	21.396	13.550

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500*	700	1000
Trifluoroethylene C_2HF_3	C_p°	69.45	90.33	103.05	113.93
	S°	293.09	333.84	366.43	405.22
	ΔH_f°	−495.80	−497.23	−497.98	−498.36
	$\log K_{p,f}^\circ$	81.721	47.145	32.292	21.146
Tetrafluoroethylene C_2F_4	C_p°	80.71	100.37	111.75	120.75
	S°	300.45	346.73	382.50	424.05
	ΔH_f°	−658.56	−658.19	−657.68	−656.76
	$\log K_{p,f}^\circ$	108.558	62.701	43.062	28.357
Fluorobenzene C_6H_5F	C_p°	95.06	150.79	187.02	219.99
	S°	303.26	365.68	422.63	495.39
	ΔH_f°	−116.65	−123.80	−128.03	−130.83
	$\log K_{p,f}^\circ$	11.973	3.620	−0.137	3.035
Hexafluorobenzene C_6F_6	C_p°	157.15	204.10	231.92	253.68
	S°	384.22	476.43	549.94	636.80
	ΔH_f°	−956.63	−954.08	−951.48	−947.68
	$\log K_{p,f}^\circ$	153.026	86.473	58.030	36.782
Chloromethane CH_3Cl	C_p°	40.88	55.19	66.65	78.91
	S°	234.76	259.03	279.53	305.47
	ΔH_f°	−86.36	−91.38	−94.93	−98.03
	$\log K_{p,f}^\circ$	10.924	4.756	1.979	−0.182
Dichloromethane CH_2Cl_2	C_p°	51.30	66.40	77.28	87.03
	S°	270.58	301.08	325.31	354.68
	ΔH_f°	−95.44	−98.62	−100.67	−102.09
	$\log K_{p,f}^\circ$	11.961	5.215	2.242	−0.028
Chloroform (trichloromethane) $CHCl_3$	C_p°	65.94	80.92	88.99	95.65
	S°	296.06	333.63	362.25	395.26
	ΔH_f°	−101.25	−102.26	−102.47	−101.96
	$\log K_{p,f}^\circ$	11.895	4.806	1.749	−0.540

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Carbon tetrachloride CCl_4	C_p°	84.01	97.40	102.97	106.78
	S°	310.66	357.19	390.95	428.40
	ΔH_f°	−100.42	−98.53	−96.40	−93.26
	$\log K_{p,f}^\circ$	10.093	3.150	0.238	−1.888
Chloroethane C_2H_5Cl	C_p°	62.97	90.91	111.00	131.71
	S°	276.27	315.18	349.11	392.46
	ΔH_f°	−111.80	−119.12	−123.89	−127.32
	$\log K_{p,f}^\circ$	10.389	2.374	−1.250	−4.064
1,1-Dichloroethane $C_2H_4Cl_2$	C_p°	76.53	103.85	122.21	139.95
	S°	305.47	351.37	389.40	436.22
	ΔH_f°	−130.00	−135.19	−138.24	−139.87
	$\log K_{p,f}^\circ$	12.667	3.448	−0.632	−3.748
1,2-Dichloroethane $C_2H_4Cl_2$	C_p°	79.50	103.34	120.50	138.07
	S°	308.70	355.10	392.75	438.90
	ΔH_f°	−129.75	−134.81	−138.07	−140.29
	$\log K_{p,f}^\circ$	12.799	3.604	−0.467	−3.586
1,1,2-Trichloroethane $C_2H_3Cl_3$	C_p°	89.29	116.82	133.34	148.20
	S°	337.69	390.28	432.42	482.71
	ΔH_f°	−138.53	−141.75	−143.05	−142.93
	$\log K_{p,f}^\circ$	13.426	3.670	−0.581	−3.786
1,1,2,2-Tetrachloroethane $C_2H_2Cl_4$	C_p°	101.09	128.74	144.56	157.99
	S°	336.34	422.08	468.11	522.16
	ΔH_f°	−152.76	−154.18	−153.89	−151.71
	$\log K_{p,f}^\circ$	14.827	4.135	−0.466	−3.892
Pentachloroethane C_2HCl_5	C_p°	118.11	144.01	157.03	166.86
	S°	381.29	448.32	499.03	556.89
	ΔH_f°	−142.26	−141.04	−138.70	−134.52
	$\log K_{p,f}^\circ$	12.525	1.641	−2.539	−5.603

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Hexachloroethane C_2Cl_6	C_p°	136.69	160.21	170.00	176.19
	S°	397.40	473.55	529.23	591.07
	ΔH_f°	−141.38	−137.24	−132.72	−126.31
	$\log K_{p,f}^\circ$	9.801	0.068	−3.968	−6.873
1-Chloropropane C_3H_7Cl	C_p°	85.10	124.39	153.01	182.38
	S°	319.6	372.79	419.45	479.28
	ΔH_f°	−130.25	−140.12	−146.48	−150.92
	$\log K_{p,f}^\circ$	8.736	−0.643	−4.917	−8.250
2-Chloropropane C_3H_7Cl	C_p°	87.74	127.53	156.06	184.77
	S°	304.72	359.24	406.98	467.81
	ΔH_f°	−146.57	−155.90	−161.59	−165.23
	$\log K_{p,f}^\circ$	10.797	0.297	−4.439	−8.102
1-Chlorobutane C_4H_9Cl	C_p°	108.11	158.91	196.02	233.97
	S°	358.74	426.43	486.10	562.87
	ΔH_f°	−147.40	−159.79	−167.49	−172.63
	$\log K_{p,f}^\circ$	6.640	−4.012	−8.891	−12.704
2-Chlorobutane C_4H_9Cl	C_p°	109.08	160.37	198.03	236.81
	S°	360.28	428.44	488.73	566.30
	ΔH_f°	−161.63	−173.72	−181.13	−185.60
	$\log K_{p,f}^\circ$	9.195	−2.441	−7.735	−11.847
Chloroethylene C_2H_3Cl	C_p°	53.93	74.48	88.28	101.88
	S°	264.26	296.94	324.34	358.28
	ΔH_f°	35.10	31.09	28.28	25.82
	$\log K_{p,f}^\circ$	−8.982	−6.663	−5.776	−5.170
1,1-Dichloroethylene $C_2H_2Cl_2$	C_p°	67.28	87.28	99.12	110.00
	S°	288.49	327.98	359.41	396.73
	ΔH_f°	1.21	−0.75	−1.88	−2.64
	$\log K_{p,f}^\circ$	−4.233	−4.212	−4.250	−4.302

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
cis-1,2-Dichloroethylene $C_2H_2Cl_2$	C_p°	65.31	86.06	98.49	109.75
	S°	289.95	328.61	359.70	396.89
	ΔH_f°	1.84	−0.42	−1.76	−2.64
	$\log K_{p,f}^\circ$	−4.266	−4.211	−4.244	−4.294
trans-1,2-Dichloroethylene $C_2H_2Cl_2$	C_p°	66.90	86.40	98.62	109.79
	S°	290.33	329.45	360.62	397.81
	ΔH_f°	4.14	2.05	0.75	−0.13
	$\log K_{p,f}^\circ$	−4.647	−4.426	−4.384	−4.377
Tetrachloroethylene C_2Cl_4	C_p°	95.10	111.84	120.00	125.81
	S°	341.46	394.43	433.50	477.44
	ΔH_f°	−14.23	−12.13	−10.17	−7.70
	$\log K_{p,f}^\circ$	−3.607	−4.539	−4.874	−5.076
Chlorobenzene C_6H_5Cl	C_p°	98.62	152.67	187.69	219.58
	S°	314.09	377.94	435.30	508.15
	ΔH_f°	51.76	44.94	40.79	37.95
	$\log K_{p,f}^\circ$	−17.311	−13.925	−12.644	−11.765
Hexachlorobenzene C_6Cl_6	C_p°	175.85	219.74	243.43	260.83
	S°	442.29	543.50	621.58	711.74
	ΔH_f°	−33.85	−29.16	−24.64	−18.66
	$\log K_{p,f}^\circ$	−7.776	−10.003	−10.813	−11.303
Bromomethane CH_3Br	C_p°	42.55	56.74	67.74	79.50
	S°	246.10	271.25	292.17	318.44
	ΔH_f°	−37.74	−57.95	−61.34	−64.27
	$\log K_{p,f}^\circ$	4.891	1.299	−0.479	−1.885
Bromoethane C_2H_5Br	C_p°	64.77	92.01	111.84	132.17
	S°	287.90	327.65	361.92	405.47
	ΔH_f°	−64.14	−86.73	−91.34	−94.64
	$\log K_{p,f}^\circ$	4.539	−0.967	−3.622	−5.707

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
1,2-Dibromoethane $C_2H_4Br_2$	C_p°	85.56	112.13	130.54	149.79
	S°	330.28	380.49	421.37	471.41
	ΔH_f°	−39.04	−73.68	−75.19	−74.22
	$\log K_{p,f}^\circ$	1.810	−2.666	−4.890	−6.571
1-Bromopropane C_3H_7Br	C_p°	86.73	125.60	141.25	182.84
	S°	331.41	385.26	432.25	492.37
	ΔH_f°	−88.03	−113.18	−119.41	−123.68
	$\log K_{p,f}^\circ$	3.840	−3.410	−6.878	−9.604
2-Bromopropane C_3H_7Br	C_p°	89.16	128.70	156.86	185.18
	S°	316.60	371.83	419.86	480.95
	ΔH_f°	−97.19	−121.84	−127.40	−130.92
	$\log K_{p,f}^\circ$	4.667	−3.209	−6.927	−9.824
1-Bromobutane C_4H_9Br	C_p°	109.75	160.12	196.82	234.43
	S°	370.54	438.90	498.94	575.97
	ΔH_f°	−107.49	−135.06	−142.72	−147.74
	$\log K_{p,f}^\circ$	2.114	−6.539	−10.681	−13.938
2-Bromobutane C_4H_9Br	C_p°	111.21	162.84	200.25	238.20
	S°	371.00	440.37	501.45	579.69
	ΔH_f°	−120.25	−147.40	−154.43	−158.41
	$\log K_{p,f}^\circ$	4.390	−5.171	−9.675	−13.184
Bromoethylene C_2H_3Br	C_p°	55.69	75.60	89.04	102.34
	S°	275.81	309.20	336.94	371.08
	ΔH_f°	78.28	58.99	56.32	53.97
	$\log K_{p,f}^\circ$	−14.059	−9.544	−7.822	−6.588
Bromobenzene C_6H_5Br	C_p°	98.28	151.88	187.19	219.24
	S°	325.01	388.53	445.68	518.31
	ΔH_f°	104.89	82.38	78.03	75.02
	$\log K_{p,f}^\circ$	−24.152	−17.890	−15.494	−13.783

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Iodomethane CH_3I	C_p°	44.27	58.37	68.95	80.33
	S°	254.30	280.37	301.75	328.40
	ΔH_f°	−13.89	−22.80	−24.94	−27.57
	$\log K_{p,f}^\circ$	−2.727	−2.407	−3.103	−3.691
Iodoethane C_2H_5I	C_p°	66.19	92.59	112.13	132.42
	S°	296.73	337.02	371.46	415.09
	ΔH_f°	−8.45	−46.69	−51.25	−54.52
	$\log K_{p,f}^\circ$	−3.745	−5.064	−6.523	−7.710
1-Iodopropane C_3H_7I	C_p°	90.21	127.70	155.52	184.22
	S°	336.64	391.83	439.45	500.11
	ΔH_f°	−30.67	−71.17	−77.03	−80.92
	$\log K_{p,f}^\circ$	−4.926	−7.862	−10.072	−11.845
Iodobenzene C_6H_5I	C_p°	101.34	154.22	188.61	220.08
	S°	334.68	399.61	457.39	530.45
	ΔH_f°	162.46	124.64	120.62	117.91
	$\log K_{p,f}^\circ$	−32.721	−22.130	−18.468	−15.800
Nitrogen-Containing Compounds					
Amines					
Methylamine CH_5N	C_p°	50.25	70.00	86.86	105.69
	S°	242.92	273.22	299.57	333.93
	ΔH_f°	−23.10	−30.92	−36.19	−40.33
	$\log K_{p,f}^\circ$	−5.672	−7.522	−8.521	−9.380
Ethylamine C_2H_7N	C_p°	72.97	106.44	131.67	158.49
	S°	285.31	330.70	370.74	422.54
	ΔH_f°	−46.15	−56.15	−62.43	−66.82
	$\log K_{p,f}^\circ$	−6.576	−10.103	−11.870	−13.321
Propylamine C_3H_9N	C_p°	96.15	140.54	174.47	210.08
	S°	324.80	384.64	437.60	506.22
	ΔH_f°	−72.51	−84.98	−92.76	−97.91
	$\log K_{p,f}^\circ$	−7.050	−12.491	−15.141	−17.281

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Butylamine $C_4H_{11}N$	C_p°	119.03	175.02	217.48	261.67
	S°	363.76	438.11	504.09	589.65
	ΔH_f°	−92.22	−107.07	−116.27	−122.13
	$\log K_{p,f}^\circ$	−8.716	−15.605	−18.935	−21.613
2-Butylamine (*sec*-butylamine) $C_4H_{11}N$	C_p°	117.65	175.56	218.99	261.67
	S°	351.79	425.93	492.29	578.40
	ΔH_f°	−104.35	−119.29	−128.28	−133.64
	$\log K_{p,f}^\circ$	−7.229	−14.966	−18.658	−21.599
3-Butylamine $C_4H_{11}N$	C_p°	120.46	180.96	224.05	266.90
	S°	338.65	414.97	483.13	570.82
	ΔH_f°	−120.04	−134.10	−142.00	−146.06
	$\log K_{p,f}^\circ$	−5.183	−13.991	−18.111	−21.346
Dimethylamine C_2H_7N	C_p°	69.37	104.31	131.46	159.79
	S°	273.42	317.23	356.85	408.82
	ΔH_f°	−18.95	−29.54	−36.11	−40.29
	$\log K_{p,f}^\circ$	−11.932	−13.584	−14.562	−15.423
Diethylamine $C_4H_{11}N$	C_p°	116.27	173.59	217.78	263.22
	S°	352.96	426.10	491.91	577.77
	ΔH_f°	−72.55	−87.86	−97.19	−102.76
	$\log K_{p,f}^\circ$	−12.704	−18.238	−20.997	−23.245
Trimethylamine C_3H_9N	C_p°	92.26	140.71	176.94	213.30
	S°	289.37	348.19	401.62	471.33
	ΔH_f°	−24.02	−36.82	−44.31	−48.53
	$\log K_{p,f}^\circ$	−17.349	−19.426	−20.635	−21.682
Triethylamine $C_6H_{15}N$	C_p°	161.75	243.09	304.50	367.36
	S°	406.43	508.61	600.74	700.74
	ΔH_f°	−99.83	−119.96	−131.96	−138.66
	$\log K_{p,f}$	−19.425	−27.011	−30.767	−33.811

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Ethyleneamine C_2H_5N	C_p°	52.84	85.86	108.99	131.59
	S°	250.96	286.06	318.86	361.83
	ΔH_f°	125.30	115.10	110.37	107.49
	$\log K_{p,f}^\circ$	−31.046	−22.718	−19.352	−16.919
Pyrrolidine C_4H_9N	C_p°	81.71	143.89	189.20	233.63
	S°	310.03	366.85	422.92	498.48
	ΔH_f°	−3.77	−19.62	−28.87	−34.14
	$\log K_{p,f}^\circ$	−20.091	−20.856	−21.578	−22.293
Pyridine C_5H_5N	C_p°	78.66	130.16	165.02	197.36
	S°	283.30	336.18	385.93	450.74
	ΔH_f°	140.08	131.88	127.19	124.52
	$\log K_{p,f}^\circ$	−33.171	−23.679	−19.812	−16.999
Aniline C_6H_7N	C_p°	109.08	170.75	210.54	247.61
	S°	319.87	390.99	455.26	537.14
	ΔH_f°	86.73	77.61	72.38	69.08
	$\log K_{p,f}^\circ$	−29.109	−23.363	−21.123	−19.545
α-Picoline (2-methylpyridine) C_6H_7N	C_p°	100.63	162.42	206.15	248.28
	S°	325.64	392.21	454.26	535.47
	ΔH_f°	98.83	87.91	81.38	77.57
	$\log K_{p,f}^\circ$	−30.909	−24.374	−21.846	−20.074
β-Picoline (3-methylpyridine) C_6H_7N	C_p°	100.16	162.09	205.81	247.82
	S°	325.60	391.96	453.88	534.97
	ΔH_f°	106.02	95.02	88.41	84.52
	$\log K_{p,f}^\circ$	−32.164	−25.130	−22.392	−20.463
		Nitriles			
Acetonitrile C_2H_3N	C_p°	52.38	69.41	83.26	98.32
	S°	243.80	274.64	300.29	332.71
	ΔH_f°	87.82	83.64	80.46	77.53
	$\log K_{p,f}^\circ$	−18.407	−12.418	−9.967	−8.199

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Acrylonitrile C_3H_3N	C_p°	64.02	87.65	104.18	120.83
	S°	274.34	312.88	345.18	385.35
	ΔH_f°	184.89	181.42	178.82	176.40
	$\log K_{p,f}^\circ$	−34.014	−21.245	−15.866	−11.890
Propionitrile C_3H_5N	C_p°	72.59	102.59	125.27	149.37
	S°	287.06	331.62	369.91	418.94
	ΔH_f°	50.54	43.64	38.79	34.94
	$\log K_{p,f}^\circ$	−16.789	−13.481	−12.248	−11.425
Butyronitrile C_4H_7N	C_p°	97.40	138.28	169.49	201.75
	S°	326.10	385.68	437.44	503.75
	ΔH_f°	33.93	24.85	18.87	14.60
	$\log K_{p,f}^\circ$	−18.994	−16.912	−16.256	−15.886
Isobutyronitrile C_4H_7N	C_p°	96.78	139.45	170.75	202.51
	S°	313.93	373.80	425.97	492.67
	ΔH_f°	25.27	16.32	10.54	6.57
	$\log K_{p,f}^\circ$	−18.120	−16.640	−16.236	−16.049
Benzonitrile C_7H_5N	C_p°	109.66	166.73	204.14	238.82
	S°	321.75	391.96	454.47	533.63
	ΔH_f°	218.74	212.67	208.91	206.19
	$\log K_{p,f}^\circ$	−45.464	−30.424	−24.131	−19.488
Nitromethane CH_3NO_2	C_p°	57.57	81.84	100.00	117.86
	S°	275.39	310.66	341.29	380.20
	ΔH_f°	−74.81	−80.83	−84.14	−85.69
	$\log K_{p,f}^\circ$	1.137	−4.267	−6.728	−8.634
Nitrocompaunds					
Nitroethane $C_2H_5NO_2$	C_p°	78.58	116.82	143.85	170.16
	S°	315.93	365.47	409.32	465.43
	ΔH_f°	−101.38	109.91	−114.47	−116.52
	$\log K_{p,f}^\circ$	0.748	−6.586	−9.934	−12.527

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
1-Nitropropane $C_3H_7NO_2$	C_p°	102.59	451.63	187.15	222.00
	S°	356.31	420.66	477.69	550.78
	ΔH_f°	−124.81	−135.65	−141.59	−144.22
	$\log K_{p,f}^\circ$	−0.190	−9.230	−13.367	−16.575
2-Nitropropane $C_3H_7NO_2$	C_p°	101.96	152.80	188.41	222.76
	S°	348.36	412.96	470.41	543.84
	ΔH_f°	−140.29	−151.00	−156.69	−159.08
	$\log K_{p,f}^\circ$	2.090	−8.027	−12.619	−16.163
1-Nitrobutane $C_4H_9NO_2$	C_p°	125.48	186.10	230.16	273.59
	S°	395.26	474.13	544.17	634.17
	ΔH_f°	−144.10	−157.32	−164.68	−168.08
	$\log K_{p,f}^\circ$	−1.929	−12.388	−17.193	−20.928
2-Nitrobutane $C_4H_9NO_2$	C_p°	124.10	186.65	231.67	275.98
	S°	384.13	462.83	533.21	623.88
	ΔH_f°	−163.76	−177.07	−184.18	−187.02
	$\log K_{p,f}^\circ$	0.914	−10.919	−16.310	−20.477
Methyl nitrite CH_3NO_2	C_p°	63.47	87.91	105.94	123.51
	S°	284.72	323.09	356.10	396.69
	ΔH_f°	−64.06	−68.91	−71.00	−70.79
	$\log K_{p,f}^\circ$	−0.243	−4.865	−6.955	−8.550
Nitrates					
Methyl nitrate CH_3NO_3	C_p°	76.73	104.39	124.22	143.05
	S°	302.38	348.36	386.81	434.59
	ΔH_f°	−120.58	−125.39	−127.19	−126.40
	$\log K_{p,f}^\circ$	5.154	−3.405	−7.177	−10.024
Ethyl nitrate $C_2H_5NO_3$	C_p°	97.74	139.37	168.07	195.35
	S°	348.95	409.15	460.91	525.85
	ΔH_f°	−154.05	−161.42	−164.47	−164.18
	$\log K_{p,f}^\circ$	6.290	−4.684	−9.550	−13.239

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Propyl nitrate $C_3H_7NO_3$	C_p°	121.75	174.18	211.38	247.19
	S°	386.10	461.16	526.05	608.02
	ΔH_f°	−174.18	−183.80	−188.24	−188.57
	$\log K_{p,f}^\circ$	4.603	−7.844	−13.398	−17.628
Isopropyl nitrate $C_3H_7NO_3$	C_p°	121.13	175.35	212.63	247.94
	S°	373.97	449.28	514.59	596.93
	ΔH_f°	−191.13	−200.66	−204.85	−204.85
	$\log K_{p,f}^\circ$	6.919	−6.706	−12.760	−17.358
Sulphur-Containing Compounds					
Dialkyl Sulphides					
Dimethyl sulphide C_2H_6S	C_p°	74.35	101.42	123.18	147.15
	S°	286.31	330.83	368.53	416.77
	ΔH_f°	−37.61	−50.71	−59.41	−119.08
	$\log K_{p,f}^\circ$	−1.259	−4.254	−5.899	−7.666
Ethylmethyl sulphide C_3H_8S	C_p°	95.58	135.70	167.08	200.79
	S°	334.11	392.58	443.47	509.10
	ΔH_f°	−59.81	−75.56	−85.61	−145.71
	$\log K_{p,f}^\circ$	−2.061	−6.680	−9.085	−11.443
Diethyl sulphide $C_4H_{10}S$	C_p°	117.53	170.50	212.59	258.53
	S°	368.78	441.54	505.89	589.90
	ΔH_f°	−83.64	−101.80	−113.01	−172.38
	$\log K_{p,f}^\circ$	−3.204	−9.566	−12.775	−15.747
Isopropylmethyl sulphide $C_4H_{10}S$	C_p°	117.65	170.37	211.92	260.62
	S°	360.03	432.83	497.06	581.28
	ΔH_f°	−90.58	−108.74	−120.00	−179.20
	$\log K_{p,f}^\circ$	−2.452	−9.296	−12.713	−15.342
1-Propylmethyl sulphide $C_4H_{10}S$	C_p°	117.86	169.91	211.00	255.81
	S°	372.46	445.22	509.19	592.50
	ΔH_f°	−81.92	−100.12	−111.50	−171.54
	$\log K_{p,f}^\circ$	−3.311	−9.552	−12.713	−15.657

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Diisopropyl sulphide $C_6H_{14}S$	C_p°	170.08	247.57	301.67	356.64
	S°	416.56	522.58	615.01	732.49
	ΔH_f°	141.46	162.80	175.64	236.81
	$\log K_{p,f}^\circ$	−4.902	−15.396	−20.450	−24.843
Dipropyl sulphide $C_6H_{14}S$	C_p°	161.96	239.12	302.04	372.59
	S°	449.36	550.57	641.45	761.74
	ΔH_f°	−125.56	−148.78	−162.55	−221.25
	$\log K_{p,f}^\circ$	−5.952	−15.395	−20.047	−24.131
Dibutyl sulphide $C_8H_{18}S$	C_p°	207.94	308.11	388.02	475.76
	S°	527.81	658.10	775.04	929.10
	ΔH_f°	−167.61	−195.64	−212.21	−272.38
	$\log K_{p,f}^\circ$	−8.799	−21.320	−27.412	−32.628
Dipentyl sulphide $C_{10}H_{22}S$	C_p°	253.93	377.10	474.01	578.98
	S°	605.97	765.34	908.30	1096.17
	ΔH_f°	−208.81	−241.71	−261.12	−322.71
	$\log K_{p,f}^\circ$	−11.792	−27.339	−34.848	−41.179
Dialkyl Disulphides					
Dimethyl disulphide $C_2H_6S_2$	C_p°	94.60	124.68	148.16	172.84
	S°	337.23	392.84	438.69	496.01
	ΔH_f°	−24.27	−41.51	−52.26	−165.85
	$\log K_{p,f}^\circ$	−2.605	−4.769	−6.177	−8.155
Diethyl disulphide $C_4H_{10}S_2$	C_p°	141.88	196.98	236.69	276.02
	S°	415.39	501.37	574.34	665.88
	ΔH_f°	−74.81	−96.32	−109.33	−223.97
	$\log K_{p,f}$	−3.981	−9.805	−12.884	−16.154
Dipropyl disulphide $C_6H_{14}S_2$	C_p°	186.19	265.68	326.35	389.95
	S°	496.14	610.57	710.11	837.89
	ΔH_f°	−117.40	−143.97	−159.49	−273.47
	$\log K_{p,f}^\circ$	−6.606	−15.557	−20.098	−24.494

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
Dibutyl disulphide $C_8H_{18}S_2$	C_p°	232.17	334.68	412.33	493.13
	S°	574.30	717.77	843.37	1004.95
	ΔH_f°	−158.70	−190.04	−208.41	−323.84
	$\log K_{p,f}^\circ$	−9.599	−21.576	−27.534	−33.045
Dipentyl disulphide $C_{10}H_{22}S_2$	C_p°	278.15	403.67	498.31	596.35
	S°	652.49	825.04	976.71	1172.06
	ΔH_f°	−199.95	−236.10	−257.36	−374.22
	$\log K_{p,f}^\circ$	−12.590	−27.593	−34.968	−41.595
Thiacycloalkanes					
Thiacyclopropane C_2H_4S	C_p°	53.97	81.84	100.25	118.13
	S°	255.60	290.12	320.79	359.78
	ΔH_f°	82.13	70.96	63.93	5.36
	$\log K_{p,f}^\circ$	−16.885	−11.484	−9.474	−8.466
Thiacyclobutane C_3H_6S	C_p°	69.71	111.13	140.96	170.16
	S°	285.68	331.37	373.80	429.40
	ΔH_f°	61.00	46.15	36.94	−22.59
	$\log K_{p,f}^\circ$	−18.766	−14.953	−13.716	−13.325
Thiacyclopentane C_4H_8S	C_p°	91.42	146.61	184.93	222.34
	S°	309.95	370.28	426.10	498.82
	ΔH_f°	−33.97	−51.17	−61.59	−121.63
	$\log K_{p,f}^\circ$	−8.095	−10.972	−12.658	−14.480
Thiacyclohexane $C_5H_{10}S$	C_p°	108.91	187.15	245.64	302.67
	S°	323.97	398.40	471.24	569.23
	ΔH_f°	−63.47	−83.14	−92.51	−146.15
	$\log K_{p,f}^\circ$	−9.358	−14.877	−17.015	−19.476
Thiacycloalkenes					
Thiophene C_4H_4S	C_p°	73.30	114.93	141.17	165.44
	S°	279.32	327.23	370.41	425.18
	ΔH_f°	115.65	105.14	98.87	41.46
	$\log K_{p,f}^\circ$	−22.082	−14.332	−11.292	−9.490

Table A.23 (*continued*)

Substance		Temperature, K			
		300	500	700	1000
2-Methylthiophene C_5H_6S	C_p°	92.90	146.48	181.25	214.64
	S°	321.21	382.67	437.86	508.57
	ΔH_f°	83.55	70.25	61.97	3.05
	$\log K_{p,f}^\circ$	−21.441	−16.009	−14.040	−13.082
3-Methylthiophene C_5H_6S	C_p°	95.40	145.98	179.70	211.67
	S°	321.92	383.21	438.06	508.02
	ΔH_f°	82.68	69.29	60.79	1.21
	$\log K_{p,f}^\circ$	−21.251	−15.882	−13.943	13.017
Thiols (Mercaptans)					
Methanethiol CH_4S	C_p°	50.42	66.57	79.62	94.06
	S°	255.39	285.01	309.57	340.54
	ΔH_f°	−23.05	−33.85	−41.21	−100.46
	$\log K_{p,f}^\circ$	1.715	−0.192	−1.314	−2.665
Ethanethiol C_2H_6S	C_p°	72.97	101.92	124.18	148.03
	S°	296.56	340.87	378.86	427.44
	ΔH_f°	−46.19	−59.37	−67.86	−14.31
	$\log K_{p,f}^\circ$	0.770	−2.826	−4.727	−6.681
1-Propanethiol C_3H_8S	C_p°	95.19	136.23	168.91	205.06
	S°	337.02	395.51	446.77	513.46
	ΔH_f°	−67.99	−83.68	−93.47	−152.51
	$\log K_{p,f}^\circ$	−0.456	−5.649	−8.296	−10.823
2-Propanethiol C_3H_8S	C_p°	96.40	138.32	168.95	200.50
	S°	324.93	384.38	436.06	502.04
	ΔH_f°	−76.36	−91.63	−101.21	−160.92
	$\log K_{p,f}^\circ$	0.370	−5.396	−8.277	−10.982
1-Butanethiol $C_4H_{10}S$	C_p°	118.70	171.84	214.93	263.38
	S°	375.97	449.36	514.34	599.61
	ΔH_f°	−88.24	−106.15	−116.98	−175.31
	$\log K_{p,f}^\circ$	−2.027	−8.702	−12.037	−15.089

Table A.23 (*concluded*)

Substance		Temperature, K			
		300	500*	700	1000
1-Pentanethiol $C_5H_{12}S$	C_p°	141.88	206.52	258.11	315.14
	S°	416.27	504.30	582.37	684.59
	ΔH_f°	−108.62	−128.91	−141.08	−200.07
	$\log K_{p,f}^\circ$	−3.507	−11.675	−15.709	−19.310
Benzenethiol C_6H_6S	C_p°	105.52	163.47	201.79	237.61
	S°	337.52	405.85	467.35	545.89
	ΔH_f°	111.42	98.49	90.[illegible]3	32.22
	$\log K_{p,f}^\circ$	−25.740	−18.359	−15.540	−13.935
		Thioacids			
Isothiocyanic acid CHNS	C_p°	46.48	57.65	63.64	[illegible]9.33
	S°	248.32	275.06	295.47	31[illegible]20
	ΔH_f°	127.57	121.42	117.36	60.54
	$\log K_{p,f}^\circ$	−19.639	−10.917	−7.358	−5.131
Thioacetic acid C_2H_4OS	C_p°	81.21	102.97	120.00	136.48
	S°	313.72	360.62	398.07	443.88
	ΔH_f°	−182.00	−191.42	−197.65	−255.60
	$\log K_{p,f}^\circ$	26.782	13.846	8.037	3.198

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